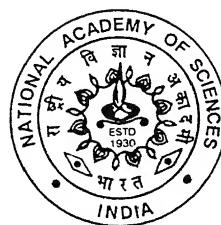


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SECTION A — PHYSICAL SCIENCES



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SECTION-A

PART IV

A comparative study on the kinetics of oxidation of unsaturated acids by quinolinium chlorochromate

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Abstract

Kinetics of oxidation of maleic acid and acrylic acid by quinolinium chlorochromate (QCC) have been investigated in acetic acid - water mixture (50% v/v) at 313 K in presence of perchloric acid medium. The order of the reaction is found to be one each with respect to QCC, substrate and H^+ for both substrates. Increase in the dielectric constant of the medium decreases the rate, while variation in ionic strength has no perceptible change in rate. The reaction rates have been determined at different temperatures and the activation parameters have been computed. Mechanism consistent with the observed results has been discussed.

(Keywords oxidation/quinolinium chlorochromate (QCC) / unsaturated acids / epoxide)

Introduction

Many oxidants like Os(VIII)¹, Ce(IV)² and Chloramine-T³ have been used for the oxidation of unsaturated acids. As a part of our earlier mechanistic investigations with

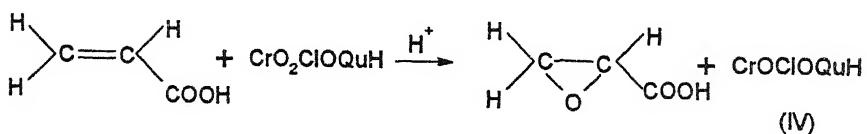
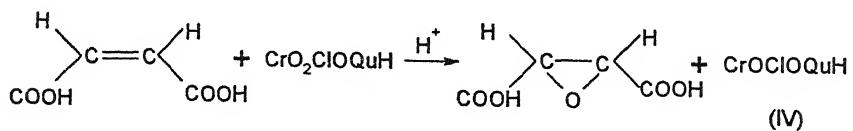
unsaturated compounds by QCC⁴, we report herein the kinetics of oxidation of unsaturated acids by QCC in acetic acid-water (1.1 v/v) solvent in presence of perchloric acid. The mechanism proposed involves slow attack of protonated QCC on the double bond of the substrate in the rate determining step and forms a very unstable complex (transient state). These complexes decompose to yield epoxides.

Materials and Method

The oxidant, quinolinium chlorochromate⁵ was synthesised according to reported procedure and its purity was checked by iodometric determination. Solutions of maleic acid (Loba) and acrylic acid (B.D.H) were always freshly prepared. Perchloric acid (E Merck) and all other chemicals (A R., B.D.H) were used without further purification.

Kinetic measurements - The reactions were performed under pseudo-first order conditions by maintaining a large excess of the substrate over oxidant. The solvent used was 50% (v/v) aqueous acetic acid. For both the acids, the progress of the reaction was followed by monitoring the decrease in [QCC] at 440 nm using systronics spectrophotometer. The optical density was measured at various intervals of time.

Stoichiometry and product analysis - Stoichiometry of the reaction for both the acids was found to be 1:1. Product analysis under kinetic conditions gave only the epoxide in each case of study, which was identified by periodate test⁶



Results and Discussion

In each case, the oxidation followed a first order kinetics both with respect to substrate and oxidant. First order plots of $\log[\text{QCC}]$ versus time were linear up to at least 75% completion of reaction. The pseudo-first order rate constants computed from the plots remain unaffected by the change in [QCC] (Table 1), establishing first order dependence of the rate on [QCC] in both the cases. At constant [QCC], the rate increases steadily with increase in [substrates] (Table 1).

The plots of $\log k_1$ versus $\log [\text{substrate}]$ are linear with unit slope (Fig. 1). The second order rate constants $k_2 = k_1/[\text{substrate}]$ gave concordant values. The plots of $1/k$ against $1/[\text{substrate}]$ gave a straight line passing through the origin (Fig. 2). This confirms first order with respect to substrate and suggests that no intermediate complex is formed between substrate and the oxidant. However, if any complex is formed its formation constant would be extremely small. Further UV-visible spectral studies did not show any evidence for the formation of QCC-substrate complex (Fig. 3 & 4).

The direct proportionality between k_1 values and $[\text{HClO}_4]$ indicate first order kinetics with respect to $[\text{H}^+]$ (Table 1). The plots of $\log k_1$ versus $\log [\text{H}^+]$ gave straight line with a slope of unity (Fig. 5). The linear increase in the rate with acidity suggests the involvement of protonated Cr(VI) species in the rate determining step, similar observations have been made for chromic acid and QFC oxidations⁷⁻⁸.

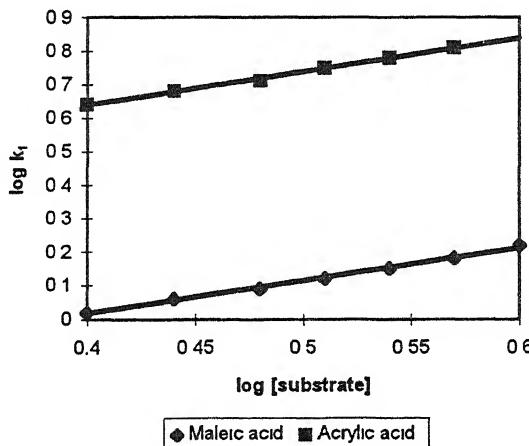


Fig. 1—Plot of $\log k_1$ vs $\log [\text{unsaturated acid}]$. $[\text{QCC}] = 1.88 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 1.15 \text{ mol dm}^{-3}$, Solvent: $\text{AcOH-H}_2\text{O} = 50\% (\text{v/v})$, Temperature = 313K

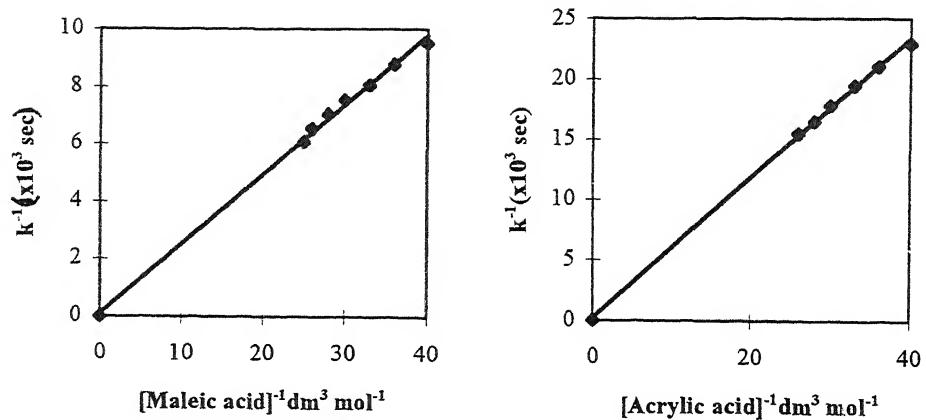


Fig 2—Plot of k^1 vs [substrate] $^{-1}$. $[QCC] = 1.88 \times 10^{-3} \text{ mol dm}^{-3}$; $[HClO_4] = 1.15 \text{ mol dm}^{-3}$, Solvent $AcOH - H_2O = 50\% \text{ (v/v)}$, Temperature = 313K

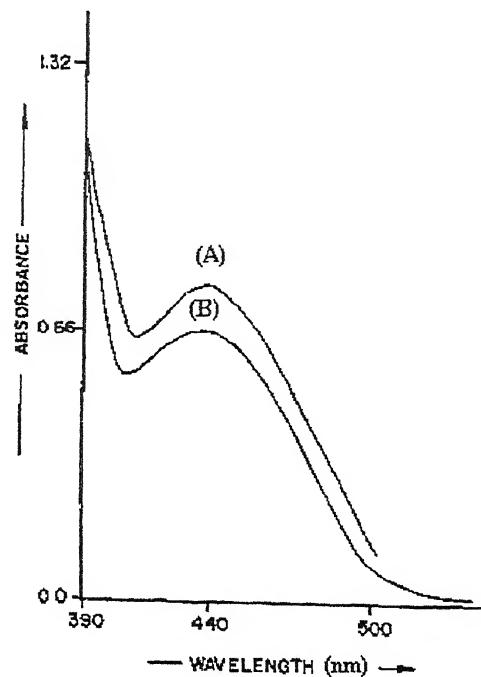


Fig 3—Electronic spectra of QCC in aqueous acetic acid 50% (v/v) without maleic acid (A) QCC in aqueous acetic acid 50% (v/v) with maleic acid (B)

Added NaClO_4 has no appreciable effect on the rate of reaction. Similar observations were also reported in oxidation of aliphatic alcohols⁹ and benzaldehydes¹⁰ by QCC. A free radical pathway in the present study is discounted. This is supported by the absence of polymerization when acrylonitrile was added to the reaction mixture.

Effect of solvent composition - The oxidation of maleic and acrylic acids were studied in the solvent containing different proportions of acetic acid and water. The reaction rate increases with increase in acetic acid content of the reaction mixture. The plots of $\log k_1$ against $1/D$ are linear with positive slope suggesting an interaction between positive ion and a dipole¹¹. This confirms the involvement of protonated oxidant species in the rate determining step.

Effect of temperature - The rate increases with the rise in temperature. The reaction between unsaturated acids and QCC were studied at four different temperatures in the range 303K-318K and the activation parameters were calculated (Table 2) from the usual relationships. The Arrhenius plots of $\log k_1$ versus $1/T$ were found to be linear (Fig. 6). The constancy of the free energies of activation may signal the operation of similar mechanism.

The reaction was found to be first order with respect to [QCC], [substrate] and $[\text{H}^+]$. Moreover the epoxides were the only reaction products observed. To explain the formation of the product and other observed data, the mechanism in Scheme I is proposed.

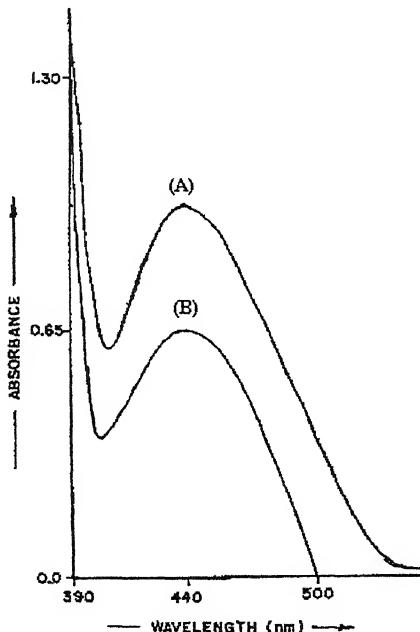


Fig. 4 - Electronic spectra of QCC in aqueous acetic acid 50% (v/v) without acrylic acid (A) QCC in aqueous acetic acid 50% (v/v) with acrylic acid (B).

Table 1- Dependence of rate on reactants at 313 K
 Solvent . AcOH - H₂O 50%(v/v)

[QCC]x10 ³ (mol dm ⁻³)	[Maleic acid] x 10 ² (mol dm ⁻³)	[Acrylic acid] x 10 ² (mol dm ⁻³)	[HClO ₄] (mol dm ⁻³)	<i>k₁</i> x10 ⁵ (s ⁻¹) Maleic acid	<i>k₁</i> x10 ⁵ (s ⁻¹) Acrylic acid
1.13	-	2.50	1.15	-	4.32
1.15	-	2.50	1.15	-	4.50
1.88	2.50	2.50	1.15	10.5	4.39
2.25	2.50	2.50	1.15	10.7	4.34
2.63	2.50	2.50	1.15	10.6	4.38
3.00	2.50	2.50	1.15	10.2	4.41
3.38	2.50	-	1.15	10.4	-
3.75	2.50	-	1.15	10.3	-
1.88	2.75	2.75	1.15	11.4	4.75
1.88	3.00	3.00	1.15	12.4	5.14
1.88	3.25	3.258	1.15	13.3	5.62
1.88	3.50	3.50	1.15	14.2	6.06
1.88	3.75	3.75	1.15	15.3	6.46
1.88	4.00	-	1.15	16.5	-
1.88	2.50	2.50	1.38	12.5	5.18
1.88	2.50	2.50	1.61	14.9	5.96
1.88	2.50	2.50	1.84	17.1	6.77
1.88	2.50	2.50	2.07	18.9	7.59
1.88	2.50	2.50	2.30	21.6	8.54

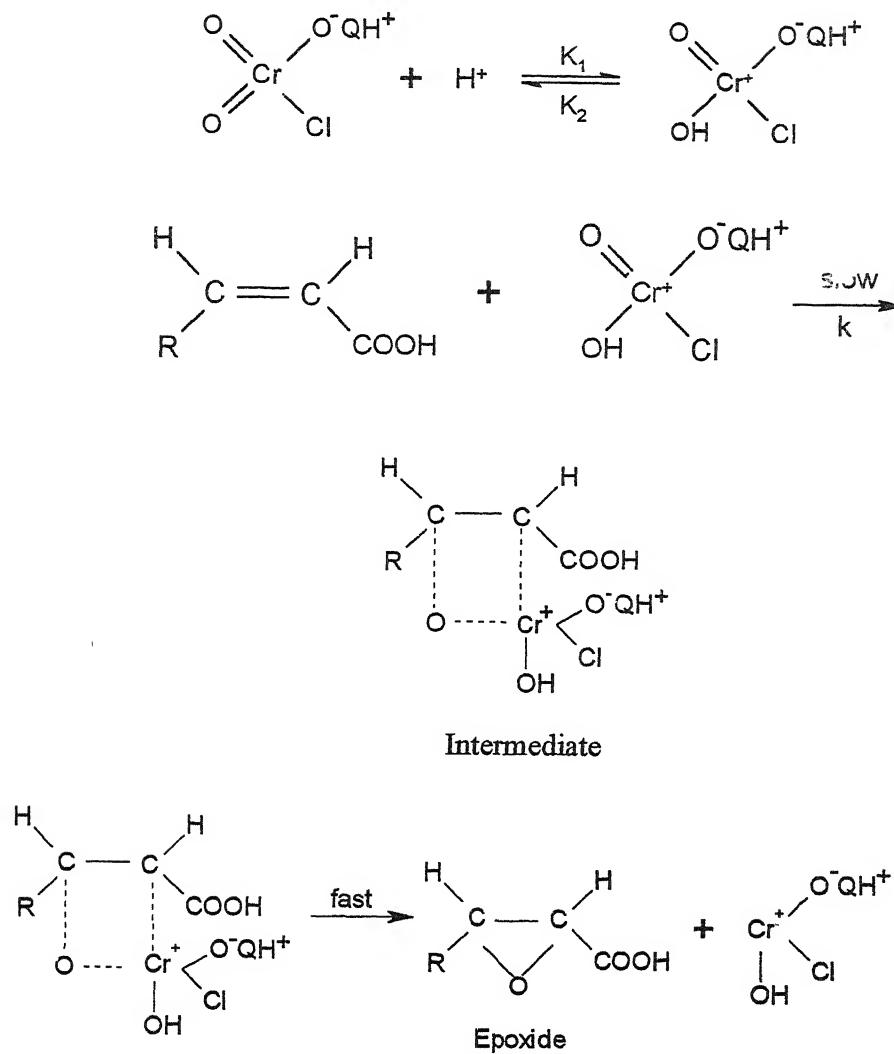


Table 2- Activation parameters.

Unsaturated acid	E_a (KJ mol ⁻¹)	$\Delta H^\#$ (KJ mol ⁻¹)	$\Delta G^\#$ (KJ mol ⁻¹)	$-\Delta S^\#$ (J/K mol ⁻¹)
Maleic acid	55.35	52.77	100.31	153.12
Acrylic acid	55.68	53.10	102.55	159.25

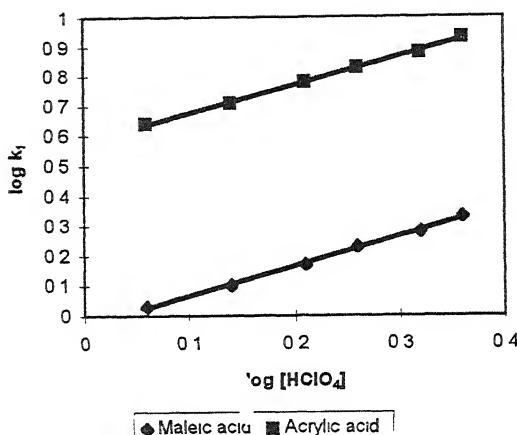


Fig 5 - Plot of $\log k_i$ vs $\log [H^+]$ $[QCC] = 1.88 \times 10^{-3}$ mol dm^{-3} , $[Unsaturated\ acid] = 2.50 \times 10^{-2}$ mol dm^{-3} , Solvent $AcOH\ H_2O = 50\% (v/v)$, Temperature = 313K

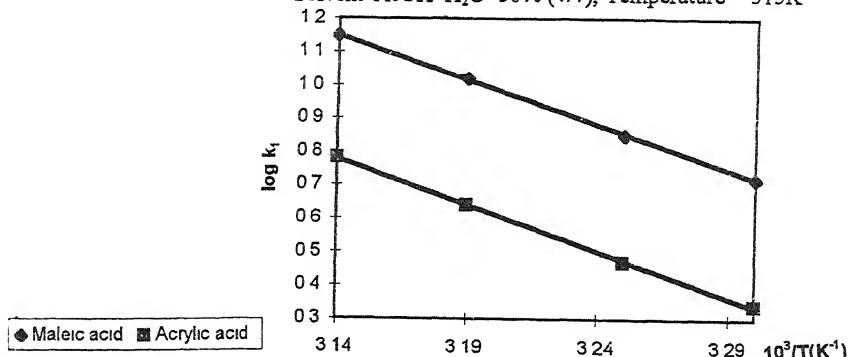
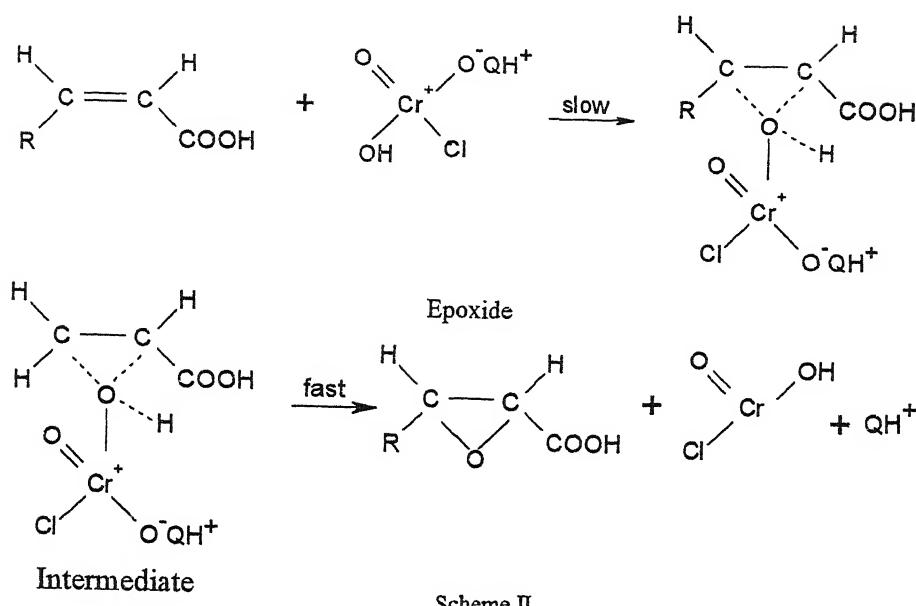


Fig 6 - Plot of $\log k_i$ vs $1/T$ $[QCC] = 1.88 \times 10^{-3}$ mol dm^{-3} , $[Unsaturated\ acid] = 2.50 \times 10^{-2}$ mol dm^{-3} , $[HClO_4] = 1.15$ mol dm^{-3} , Solvent $AcOH\ H_2O = 50\% (v/v)$,

The rate determining step may be unstable due to complex formation between the protonated QCC and substrate. An electrophilic attack of Cr(VI) being positively charged in the protonated QCC on the double bond leads to a four centre intermediate state which rearranges to give the epoxide in the final step. In the proposed mechanism (Scheme I) a direct chromium to carbon bond does not account for the insensitivity to steric effect very often observed in the oxidation of olefins by Cr(VI)¹² Thus the most favourable reaction path may be the three centre type addition as depicted in Scheme II.



where R= H for acrylic acid and R=COOH for maleic acid.

Both schemes envisage an oxygen atom transfer from the oxidant. This is in accord with the earlier observations made for unsaturated substrates¹³⁻¹⁴. A closer look on the energy of activation of the reactions under investigation reveals that values are very close indicating that the electrical and structural properties of solvent system are little affected by the presence of different substrates. The energy of activation of both the acids are nearly equal. This shows that both the acids are oxidised with similar rate. Consequently the rate law can be proposed as

$$-\frac{d[\text{QCC}]}{dt} = K_{\text{obs}} [\text{QCC}] [\text{H}^+] [\text{S}]$$

Acknowledgements

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A novel spray reagent for the detection of plant growth regulators on thin layer plates

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Abstract

Two new highly sensitive chromogenic spray reagents ($\text{AlCl}_3\text{-HClO}_4$) and ($\text{CuCl}_2\text{/HClO}_4$) have been developed for the detection of some plant growth regulators on silica gel G coated chromatoplates. The reagents produce different colours in visible light than those in u v light

(Keywords thin layer chromatography/plant growth regulators/spray reagents)

Introduction

Several spray reagents such as 2,4-dinitrophenyl hydrazine¹, ferric chloride in perchloric acid² and ceric sulphate³ in concentrated sulphuric acid have been used for the detection of indole derivatives on chromatoplates. Thomas *et al.*⁴ have used solutions of aluminium chloride, thorium chloride, basic lead acetate and neutral lead acetate for the detection of flavonoids on paper strips. Hranisavljevic *et al.*⁵ have used cupric chloride for the detection of various oximes. None of the aforesaid reagents is ultra sensitive therefore it is worthwhile to develop highly sensitive spray reagents in order to analyse the plant growth regulators which are present at a very low concentration in plants. Now the efforts are made to develop new and ultrasensitive chromogenic spray reagents. The results obtained are described in this paper.

Materials and Method

Silica Gel G, perchloric acid, benzene and ethyl acetate (Glaxo, India) and aluminium chloride (Danpha, India) were used

Preparation of chromatoplates

The plates (15 x 3.5 cm) were prepared by coating a slurry of silica gel G in water (2:2.5) with the help of an applicator. The plates were dried at room temperature for

4 h, activated at 110°C for 10-15 min, cooled at room temperature and then used for analysis

Preparation of solutions

Spray reagent I

Aluminium chloride (0.5M) was prepared by dissolving anhydrous aluminium chloride (16.63 g) in 250 ml water. The spray reagent was prepared by mixing 1 ml of this aluminium chloride solution in 50 ml of aqueous perchloric acid (35%).

Spray reagent II

Cupric chloride (1M) was prepared by dissolving anhydrous cupric chloride (16.82 g) in 125 ml of water. The spray reagent was prepared by mixing 2 ml of this cupric chloride solution with 50 ml of aqueous perchloric acid (35%).

Test solution

The solution (1%) of plant growth regulators were prepared in ether or methanol. The test solution was spotted on TLC plates, the solvent was removed, plates were developed in benzene-ethyl acetate as solvent system, dried, sprayed with $\text{AlCl}_3\text{-HClO}_4$ and $\text{CuCl}_2\text{-HClO}_4$ separately and then heated in an electric oven at 120°C for 1-2 min to reveal the spots. The colour of the spots was noted and then the plates were exposed to uv light. The colour developed under the uv light was also noted.

Results and Discussion

The R_f values, colour and the lower limit of detection of plant growth regulators by TLC are recorded in Tables 1 and 2. The results show that the spray reagents under study are highly sensitive i.e. their sensitivities are thousand times more than the previously developed reagents⁶⁻⁸ ($\text{AsCl}_3\text{-AcOH}$ and $\text{AsCl}_3\text{-HIO}_4$) for this purpose.

The advantage of these spray reagents over the previously described spray reagents is that they give different colour with different type of plant growth regulators, for example indole derivatives gave light yellow to yellowish violet colour with ($\text{AlCl}_3\text{-HClO}_4$) and yellowish brown to reddish brown colour with ($\text{CuCl}_2\text{-HClO}_4$). Naphthalene acids give blue colour with ($\text{AlCl}_3\text{-HClO}_4$) and yellow colour with ($\text{CuCl}_2\text{-HClO}_4$). Naphthols give pink colour with ($\text{AlCl}_3\text{-HClO}_4$) and grey to greyish-purple colour with ($\text{CuCl}_2\text{-HClO}_4$). Cinnamic acid derivatives like coumaric

and protocatechuic acid give brown to green colour with ($\text{AlCl}_3\text{-HClO}_4$) and green colour with ($\text{CuCl}_2\text{-HClO}_4$). However, the spray reagent ($\text{AlCl}_3\text{-HClO}_4$) is more sensitive than ($\text{CuCl}_2\text{-HClO}_4$) as it can detect low levels of plant growth regulators (Tables 1 & 2). Also the colours developed with spray reagent ($\text{AlCl}_3\text{-HClO}_4$) are stable for a longer period than that developed with ($\text{CuCl}_2\text{-HClO}_4$).

Table 1- R_f values and colour formation of various plant growth regulators with $\text{AlCl}_3\text{-HClO}_4$

Compound	R_f values in solvent system				Visible light		UV light	
	(1)	7.1 (2)	6.1 (3)	4.1 (4)	2.1 (5)	Colour (6)	Sensitivity (μg) (7)	Colour (8)
Indole acetic acid	0.11	0.12	0.13	0.13	Light yellow	0.25	Pink	0.19
Indole butyric acid	0.21	0.27	0.31	0.35	Yellowish violet	0.20	Pink	0.12
α -Naphthalene acetic acid	0.35	0.36	0.39	0.41	Blue	0.05	Yellow	0.12
β -Naphthalene acetic acid	0.34	0.36	0.36	0.37	Blue	0.05	Black	0.29
Phenyl acetic acid	0.31	0.46	0.54	0.59	Orange	0.15	Light yellow	0.08
Phenoxy acetic acid	0.28	0.37	0.40	0.42	Pink	0.30	Brown	0.18
α -Naphthol	0.76	0.78	0.80	0.80	Pink	0.32	Pink	0.26
Kinetin	0.02	0.46	0.55	0.62	Black	0.52	Brown	0.39
Coumaric acid	0.16	0.18	0.18	0.20	Brown	0.47	Brown	0.42
Protocatechuic acid	0.07	0.07	0.09	0.09	Green	0.35	Yellow	0.27
Vanillic acid	0.19	0.20	0.22	0.23	Grey	0.26	Black	0.19

Solvent system . Benzene . Ethylacetate · Spray reagent · $\text{AlCl}_3\text{-HClO}_4$

The mobile phase such as diisopropylether-dimethylformamide (4:1), n-butanolacetic acid-water (5:1:2) and acetone-chloroform-acetic acid-water (8:8.4:1) can be used for the separation of plant growth regulators. The best separations are achieved in benzene ethyl acetate.

Table 2- R_f values and colour formation of various plant growth regulators with $\text{CuCl}_2 - \text{HClO}_4$

S No	Compound	R_f values in solvent system			Visible light		U V light	
		10 l	8 l	6.1	Colour	Sensitivity ($\mu\text{g/spot}$)	Colour	Sensitivity ($\mu\text{g/spot}$)
1	2	3	4	5	6	7	8	
1	Indole acetic acid	0.28	0.34	0.41	Yellowish brown	1.0	Light green	0.5
2	Indole butyric acid	0.16	0.24	0.32	Reddish brown	1.5	Brown	1.0
3	α -Nepthalene acetic acid	0.22	0.29	0.39	Yellow	1.5	Pinkish brown	1.5
4	β -Naphthalene acetic acid	0.24	0.32	0.44	Yellow	2.0	Pinkish brown	1.0
5	Kinetin	0.65	0.69	0.74	Black	0.5	Brown	0.5
6	Gibberellic acid	0.69	0.72	0.79	Brown	1.5	Blue	1.0
7	Phenyl acetic acid	0.19	0.23	0.29	Grey	2.0	Blue	1.0
8	Phenoxy acetic acid	0.27	0.35	0.46	Greyish purple	2.5	Black	1.5
9	α -Naphthol	0.72	0.78	0.82	Light pink	1.0	Creamish yellow	0.5
10	β -Naphthol	0.74	0.82	0.84	Pinkish grey	2.0	Creamish yellow	1.0
11	Coumaric acid	0.20	0.23	0.27	Light green	0.5	Bluish green	0.25
12	Protocatechuic acid	0.10	0.14	0.19	Green	1.5	Yellow	1.0

Solvent system Benzene . Ethyl acetate (10 : 1, 8 : 1 and 6 : 1)

Spray reagent . $\text{CuCl}_2 - \text{HClO}_4$

However, decomposition of indole derivatives was observed in mobile phase containing ammonia or formic acid

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Monomer reactivities and kinetics in radical terpolymerization of α -terpineol, styrene and acrylonitrile

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Abstract

Synthesis of a series of functional terpolymers, consisting of two electron donating monomers namely α -terpineol and styrene with one electron accepting monomer namely acrylonitrile (AN), using benzoylperoxide as radical initiator in xylene at 75°C for 2 h have been carried out. The system follows ideal kinetics with an overall activation energy 37 kJ/mol. The formation of the terpolymers is confirmed by the presence of peaks between 7.2–7.6 δ due to phenyl group of styrene and at 7.8–8.0 δ due to alcoholic group of α -terpineol. ^{13}C NMR spectrum of terpolymer has peaks at 120 δ of $-\text{CN}$, 132 δ of $-\text{C}_6\text{H}_5$ and 64–66 δ of $\text{C}-\text{OH}$. Bands at 3064 cm^{-1} , 2242 cm^{-1} and 3445 cm^{-1} in the FTIR spectrum of the terpolymer have indicated the presence of phenyl, cyanide and hydroxy groups respectively. The reactivity ratios, determined by the Kelen-Tüdös method, are 1.45 for r_1 (α -terpineol + Sty) and 1.3 for r_2 (AN). The glass transition temperature (T_g), determined by DSC, is 59.6°C.

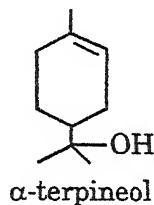
(Keywords : FTIR/ $^1\text{H}/^{13}\text{C}$ NMR spectra/ reactivity ratios / α -terpineol /styrene / acrylonitrile/ terpolymerization / kinetics)

Introduction

Despite the large amount of data accumulated for copolymerization of vinyl monomers, relatively little synthetic and kinetic information have been published on terpolymerization.^{1,2} Terpolymerization has become increasingly important from commercial view point, because it provides a convenient method for modifying polymer properties.

Styrene (Sty) and acrylonitrile (AN) are highly reactive monomers and can be homo, co-and terpolymerized with numerous other vinyl monomers^{3,4}. These monomers frequently copolymerize with isoprene^{6,7}, α -and β -pinene⁸⁻¹⁰. However, reports on the polymerization of oxygenated derivatives of terpenes except

citronellol¹¹⁻¹⁸, geraniol¹⁴, linalool¹⁵⁻¹⁶ and α -terpineol¹⁷⁻¹⁸ are still scarce. A probable reason seems to be the inability of the terpenoids to undergo homo-polymerization because of steric hinderance¹⁹⁻²⁰, low stabilization energy between monomers and free radical transition state²¹, excessive chain transfer²² or termination of cyclization²⁸. Terpenoid monomers have great relevance and can be used as functional polymers¹¹⁻¹⁸. Therefore, we have extended our studies to the synthesis and characterization of terpolymers using monocyclic monoterpenoid, α -terpineol, styrene with acrylonitrile. We have presented a discussion of the kinetics, thermal properties and characterization of terpolymers.



α -terpineol, $C_{10}H_{18}O$, the unsaturated tertiary alcohol, is susceptible to polymerization as it contains one double bond.

Materials and Method

Acrylonitrile, styrene (Merck-Schuchardt) and solvents were purified by the usual methods^{24,25}. α -Terpineol²⁶ (Fluka) was purified by fractional distillation. Benzoylperoxide (BPO) was recrystallised twice from chloroform.

Terpolymerization

The terpolymerization kinetics was followed by the dilatometric technique. The solution was prepared by taking required quantities of all the three monomers alongwith BPO in xylene as an inert solvent. Terpolymerization was carried out at $75 \pm 0.1^\circ C$ for two hours under a nitrogen blanket. The terpolymer(s) which precipitated from methanol were redissolved in xylene, reprecipitated and dried under vacuum. The terpolymer formed was treated with acetonitrile to remove polyacrylonitrile, cyclohexane to remove polystyrene, and toluene to remove copolymer(s). The rates of polymerization (R_p) were calculated from the slope of the graph between the conversion percentage and time. The monomer reactivity ratios were determined by

Kelen-Tudos method²⁷ The FTIR spectra were recorded on a Perkin-Elmer 599B spectrophotometer ¹H and ¹³C NMR spectra were recorded on a Varian 100HA/ JEOL 400 LA Spectrometer using CDCl₃ as solvent and TMS as internal reference Elemental analysis was performed on Perkin-Elmer elemental analyser at 24°C Thermogravimetric analysis (TGA) was performed on a Stanton Redcroft instrument with a heating rate of 10°C/min in nitrogen. Differential Scanning Calorimetry (DSC) was carried out using the DuPont V4 1C Model 2000 analyzer, at a heating rate of 10°C/min, with a weighing approximately 10 mg

Results and Discussion

The kinetics of terpolymerization are presented in Tables (1-2) All the reactions were associated with a short induction period between 2 and 8 min. The initiator and the monomer(s) exponent values were found to be 0.5 ± 0.01 and unity respectively

Polymerization runs were also carried out at 70°C and 85°C to evaluate the activation energy. The R_p is a direct function of temperature and the apparent activation energy, determined from the slope of the Arrhenius plot, its value is 37kJ/mol (Fig. 1)

Table 1- Effect of initiator concentration on the rate of terpolymerization

Sample	[BPO] × 10 ³ (mol l ⁻¹)	% Conversion terpolymer	R_p × 10 ⁶ (mol l ⁻¹ s ⁻¹)	[η] × 10 ² (dl/g)
1	1.83	6.2	3.71	4.2
2	5.50	8.3	5.88	4.0
3	9.18	11.8	7.58	3.7
4	12.85	13.6	9.54	3.5
5	16.52	15.5	9.92	3.3

[AN]	= 2.34 mol l ⁻¹
[Sty]	= 1.34 mol l ⁻¹
[α -trpineol]	= 0.90 mol l ⁻¹
terpolymerization time	= 2 h
terpolymerization temperature	= 75 ± 0.1°C

Table 2— Effect of monomer(s) concentration on the rate of terpolymerization of α -terpineol, styrene and acrylonitrile

Sample	α [AN] (moll^{-1})	[Styrene] (moll^{-1})	[α -terpineol] (moll^{-1})	Conversion (%)	$R_p \times 10^7$ ($\text{moll}^{-1}\text{s}^{-1}$)	$[\eta] \times 10^2$ (dl/g)
6	1.00	1.34	0.90	6.80	5.24	3.1
7	1.67	1.34	0.90	8.84	6.45	3.5
3	2.34	1.34	0.90	11.8	7.58	3.7
8	3.01	1.34	0.90	15.98	8.70	3.8
9	3.68	1.34	0.90	17.75	9.77	4.1
10	2.34	0.57	0.90	7.05	6.02	2.5
11	2.34	0.96	0.90	9.72	6.91	2.8
12	2.34	1.73	0.90	17.95	8.12	3.4
14	2.34	2.11	0.90	18.95	8.70	3.7
15	2.34	1.34	0.38	8.33	4.16	2.9
16	2.34	1.34	0.64	10.36	5.01	2.1
17	2.34	1.34	1.16	14.2	6.91	2.3
19	2.34	1.34	1.42	18.1	7.07	2.5

BPO = 9.18×10^{-3} moll^{-1}

terpolymerization time = 2 h

terpolymerization temperature = $75 \pm 0.1^\circ\text{C}$

The intrinsic viscosity (η) of the terpolymers decreases with increase in the initiator concentration and increases with increase in the comonomer concentration. These observations tend to support the view that although α -terpineol has a hydroxyl proton, it might behave also as a chain transfer agent.

Characterization of terpolymer(s) :

Solubility : The terpolymer was soluble in aprotic solvents like dimethylformamide, dioxane, carbon tetrachloride, and chloroform.

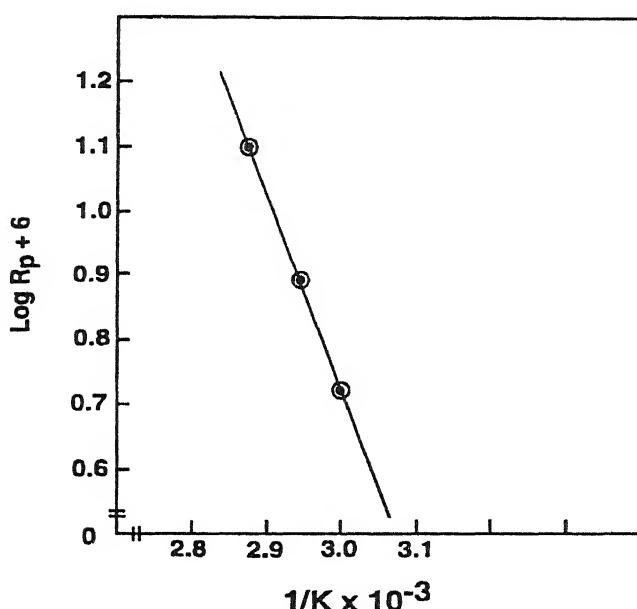


Fig. 1—Arrhenius plot of rate of polymerization versus polymerization temperature,
 $[BPO] = 9.18 \times 10^{-3} \text{ mol l}^{-1}$, $[\alpha\text{-terpineol}] = 0.909 \text{ mol l}^{-1}$, $[AN] = 2.34 \text{ mol l}^{-1}$,
 $[\text{Styrene}] = 1.34 \text{ mol l}^{-1}$, terpolymerization time = 2 h

Elemental Analysis : The percentage of nitrogen in terpolymer has been calculated from elemental analysis. The values obtained were 4.0, 4.49, 6.89, 5.61, 11.8, 12.92 percent respectively (samples 3, 6, 7, 14, 16 and 19)

FTIR spectroscopy : FTIR spectra were obtained using DMF as a solvent. The spectra consists of following groups of bands (Fig. 2).

- (i) The range of C—H stretching vibrations due to aromatic ring at $3064 - 3072 \text{ cm}^{-1}$.
- (ii) The range of C—H bending vibrations at $1451-1379 \text{ cm}^{-1}$.
- (iii) The $-\text{C}\equiv\text{N}$ band of acrylonitrile is present at 2242 cm^{-1} .
- (iv) The $-\text{OH}$ band of α -terpineol appears at 3445 cm^{-1} .

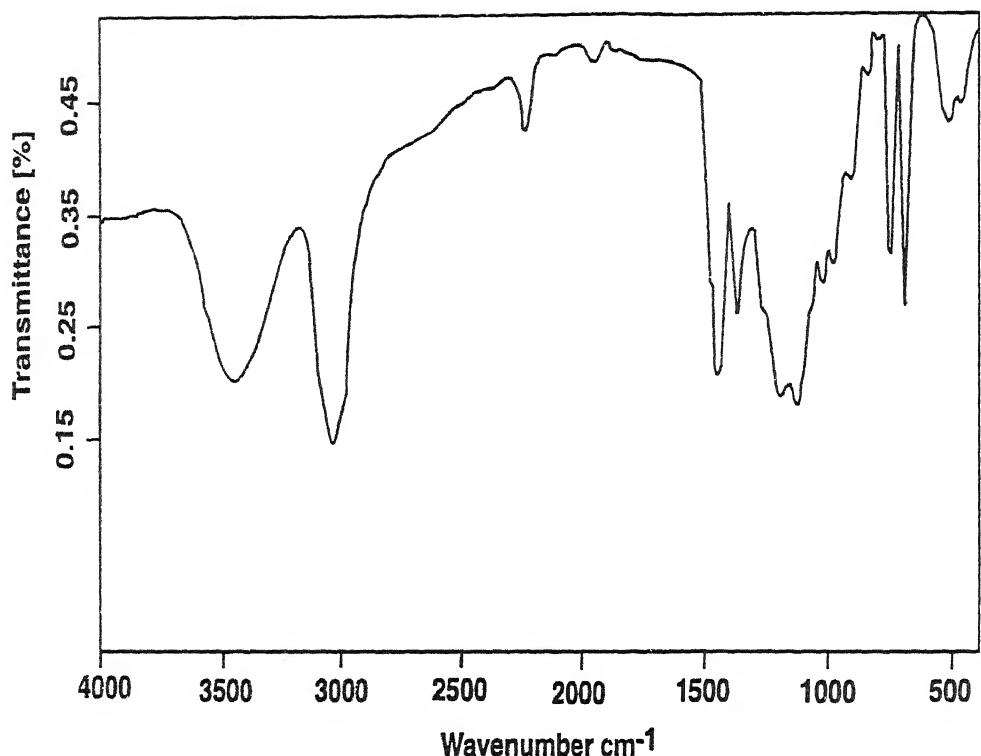


Fig 2- FTIR spectrum of the terpolymer (sample 3)

Nuclear Magnetic Resonance Spectroscopy :

The chemical shifts of protons, attached to elements other than carbon such as $-\text{OH}$, $-\text{NH}$ and $-\text{SH}$, to an extent, are influenced by the related phenomena of intermolecular exchange and hydrogen bonding. Signals appear in the NMR spectra, due to $-\text{OH}$ (hydroxyl protons) with species of small molecular weight where intermolecular association is not hindered, in the region $\delta=3\text{--}5.5$ ppm (hydroxyl proton of methanol appears at $\delta=3.3$ ppm, whereas those of ethanol appears at $\delta=5.4$ ppm)^{28,29}. However, with many large molecules, hydroxyl protons often appear near $\delta=8$ ppm even at relatively high concentration, partially due to steric effects and partially due to resonance stabilization. Therefore, the peaks of $-\text{OH}$ group appears in the range of 7.8δ to 8.0δ in the NMR spectra of α -terpineol as well as in terpolymer.

The NMR spectra of pure α -terpineol(I) and those of terpolymers (II) (Fig. 3) show the following peaks which were assigned (1H, OH) singlet at 7.7-8.0 δ , (3H, CH_3) singlet at 0.9-1.0 δ , (2H, CH_2) doublet at 4.2-4.7 δ , (1H, CH) triplet at 1.8-2.2 δ . However, an additional peak in terpolymer is assigned for (5H, C_6H_5) doublet at 7.2-7.6 δ .

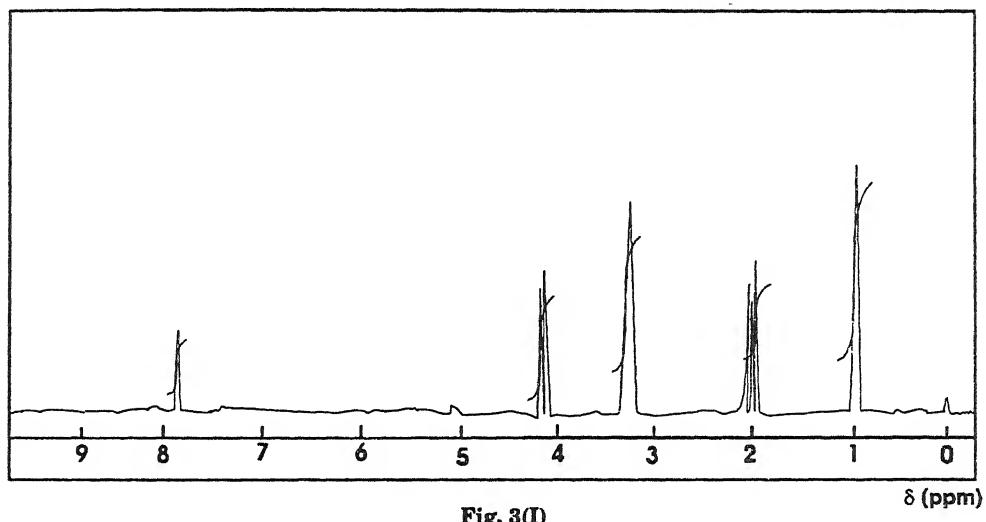
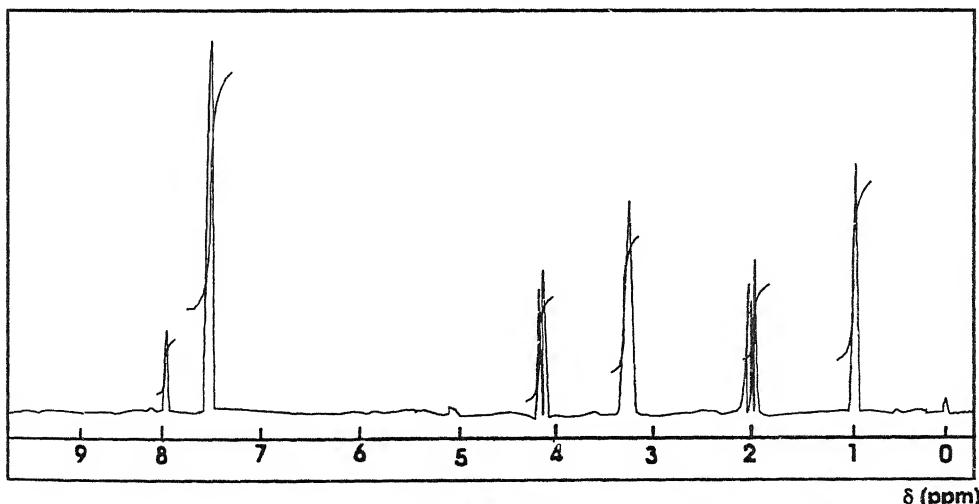


Fig. 3(I)

Fig. 3 – ^1H NMR Spectrum of the terpolymer (sample 3).

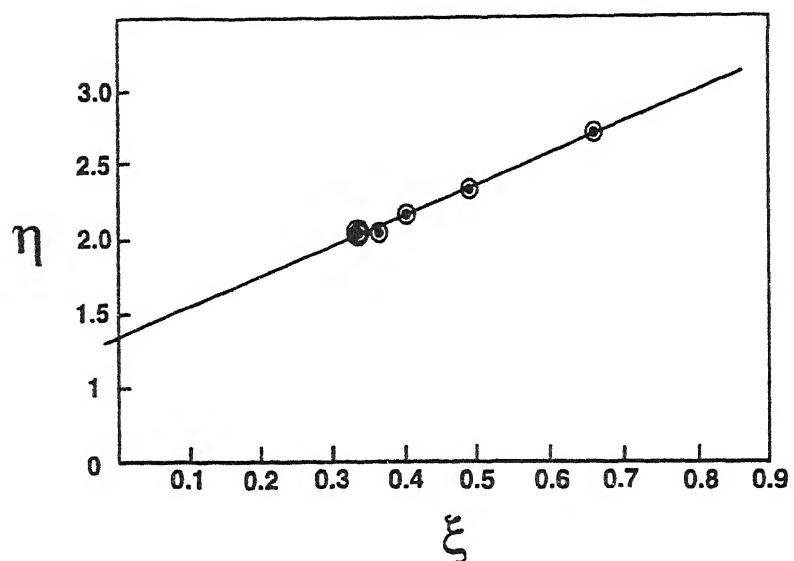


Fig. 4—Kelen-Tüdos plot of determination of reactivity ratios
 $^{13}\text{C-NMR}$

The ^{13}C spectrum of the terpolymer (Fig. 5) shows the following peaks ($-\text{CH}_3$), 21ppm, ($-\text{CH}_2$), 42ppm, ($-\text{CH}$) 52-53ppm, ($-\text{C}_6\text{H}_5$), 132ppm; tertiary C-OH 64-66ppm, ($-\text{CN}$), 120ppm.

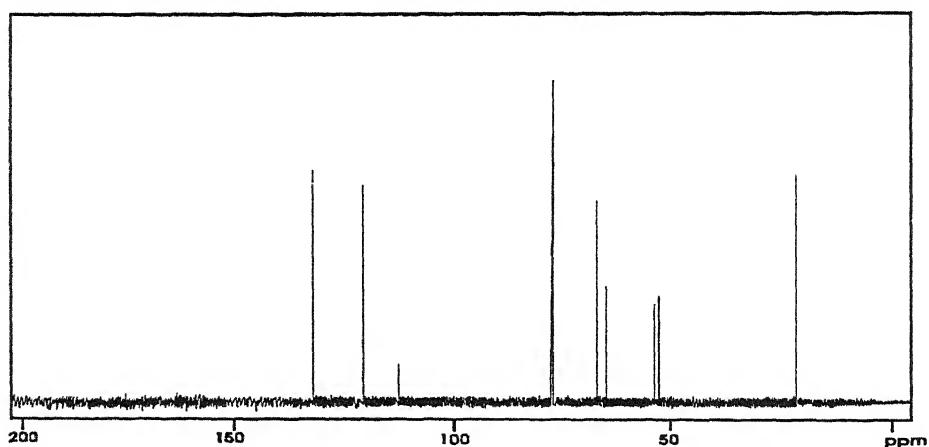


Fig. 5— ^{13}C NMR spectrum of terpolymer (sample 3).

The bands and peaks in the FTIR, ^1H NMR and ^{13}C - NMR spectra respectively, confirm the presence of styrene, acrylonitrile and α -terpineol units in the terpolymer chain

Differential Scanning Calorimetry :

The DSC scan of terpolymer (Fig. 6) showed a well pronounced endothermic transition around the temperature 59°C . The endothermic transition in the terpolymer can be attributed to the formation reaction as reported by various authors for polystyrene, polyMMA, and its terpolymers^{30,31} with terpenoids¹⁶. The values of glass transition temperature (T_g), onset temperature (T_o), and the peak temperature (T_p) are as follows .

$$T_g = 59^\circ\text{C}; T_o = 142.8; T_p = 145.6, T_p - T_o = 2.8$$

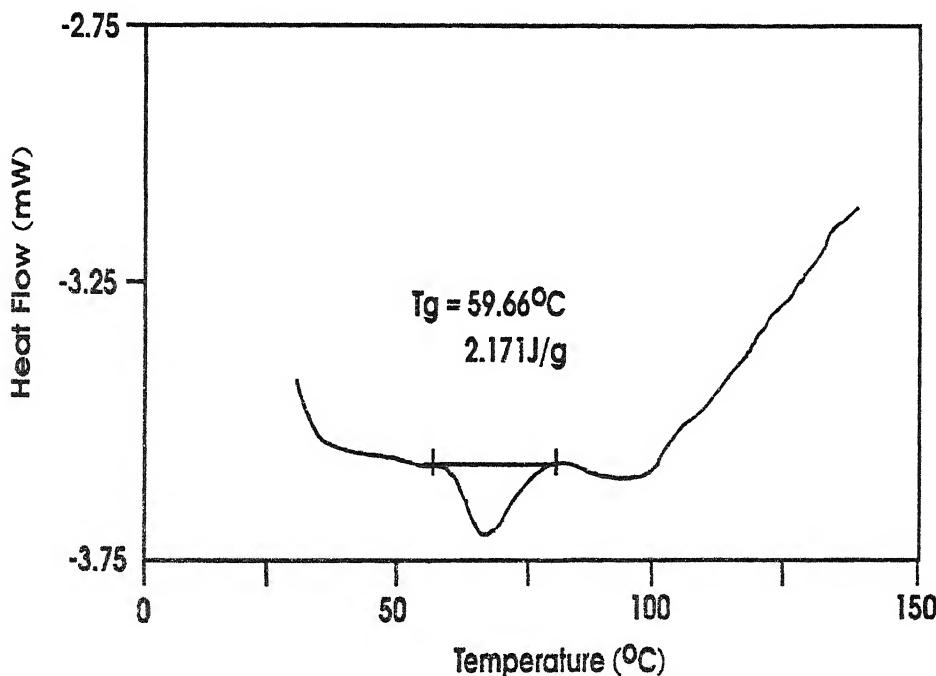


Fig. 6- DSC curve of the terpolymer (sample 3)

The onset temperature (T_o) is obtained at the intercept of the tangents to the base line at the lower temperature side of the endothermic peak. T_p is the temperature at which the bulk of the terpolymer has undergone a dehydration reaction and the difference between T_p and T_o ($T_p - T_o$) is the measure of the overall rate of reaction. The smaller the difference the greater is the rate of reaction.

Thermogravimetric Analysis

Results from thermogravimetric analysis (Fig. 7) show that the terpolymer is stable upto 370°C and rapid decomposition starts at 390°C

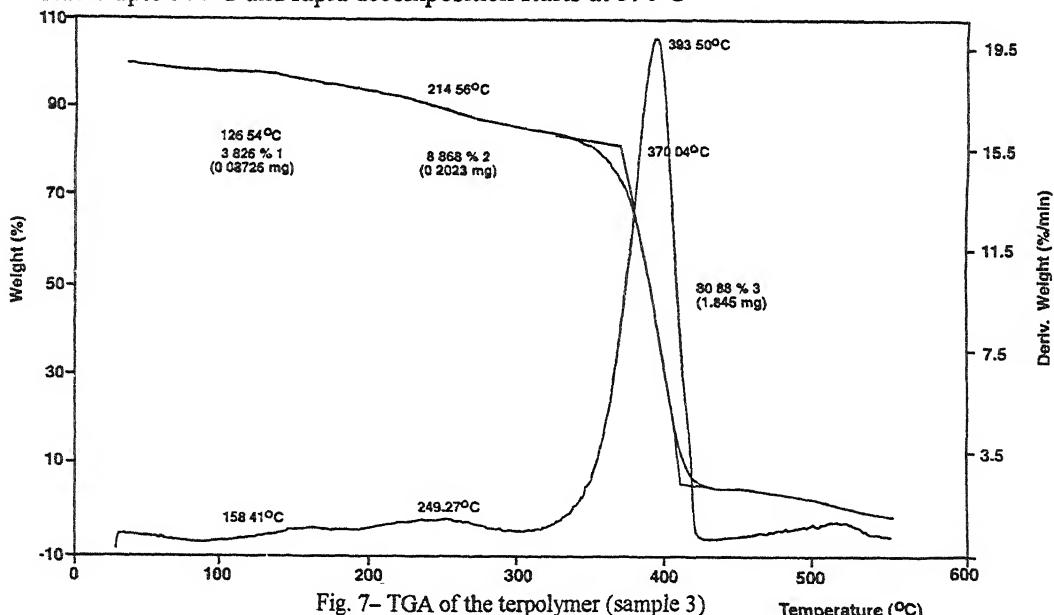


Fig. 7- TGA of the terpolymer (sample 3)

Terpolymer Composition and values of Reactivity Ratios :

The moles of [α -terpineol] and [Sty] formed have been calculated from the peak area of hydroxy (7.8–8.0 δ) and phenyl protons (7.2–7.6 δ). The moles of acrylonitrile formed have been calculated from elemental analysis (%N). The Kelen-Tüdös approach has been used for the evaluation of r_1 and r_2 for the monomer(s) as follows :

$$\eta = r_1 \xi - \frac{r_2}{\alpha} (1-\xi)$$

where $\eta = \zeta/(\alpha+H)$ and $\xi = H/(\alpha + H)$. The transformed variables G and H are given by

$$G = \frac{[M_1]/[M_2]\{d[M_1]/d[M_2] - 1\}}{d[M_1]/d[M_2]}$$

$$H = \frac{([M_1]/[M_2])^2}{d[M_1]/d[M_2]}$$

where, M_1 and M_2 are moles of styrene + α -terpeniol + AN

We have calculated the parameter α by taking the square root of the product of the lowest and highest values of H for the terpolymerization series. Graphical values of Sty+ α -terpineol/ AN yields $r_1=1.45$ and $r_2=1.3$ (Fig 4) (Table-3) The values of r_1 and r_2 favour random terpolymerization^{32,33}.

Table 3- Composition of terpolymers

Sample	Monomer feed		Mole fraction		η	ξ
	$[(\text{Sty}+\alpha\text{-terp})/\text{AN}]$	AN	[Sty]	$[\alpha\text{-terp}]$		
6	2.22	0.08	0.58	0.33	2.98	0.65
13	1.28	0.09	0.58	0.34	2.90	0.39
3	0.95	0.12	0.51	0.36	2.28	0.35
16	1.06	0.1	0.48	0.41	2.42	0.35
8	0.97	0.19	0.41	0.38	1.60	0.48
9	0.74	0.20	0.42	0.36	1.44	0.36

Conclusion

The radical terpolymerization of [AN] with [Sty+ α -terpineol] results in functional terpolymer.

Acknowledgements

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Effect of micelles on speciation of ternary complexes of uranium(VI) with oxalic and malonic acids

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Abstract

A computer assisted investigation has been carried out on the nature of ternary complexes of uranium(VI) with oxalic acid as primary ligand and malonic acid as secondary ligand. The approximate formation constants have been calculated with SCPHD from the pH metric data. The formation constants thus obtained are refined with MINIQUAD75. The selection of the best-fit chemical model is based on the statistical parameters and residual analysis. The major complexes formed are : $[\text{UO}_2(\text{C}_2\text{O}_4)(\text{H}_3\text{C}_3\text{O}_4)_2]^{2-}$, $[\text{UO}_2(\text{HC}_2\text{O}_4)(\text{H}_3\text{C}_3\text{O}_4)]$ and $[\text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_3\text{C}_3\text{O}_4)]^{3-}$. The distribution patterns of the different species with the pH values showed that $[\text{UO}_2(\text{C}_2\text{O}_4)(\text{H}_3\text{C}_3\text{O}_4)_2]^{2-}$ is the predominant species. The nonlinear trend of stabilities of the complexes with surfactant concentration is explained based on the dielectric constant of the medium, Stern layer and the electrostatic interactions.

(Keywords formation constant/ternary complexes/micelles/uranyl ion/oxalate/malonate)

Introduction

Ternary complexes of uranyl ion with biologically important ligands¹⁻⁴ and with some carboxylic acids have been studied^{5,6}. Uranyl complexes of dicarboxylic acid have also been studied in aqueous⁷⁻⁹ and in aqua-dioxane mixtures^{10,11}. The stability constants of the ternary complexes of copper(II) with malonic acid as the primary ligand and oxalic, maleic, fumaric, succinic, phthalic and salicylic acids, pyrocatechol(O,O donors), O-aminophenol, 8-quinolinol (O,N donors) and 2,2'-bipyridyl, ethylene diamine(N,N donors) as secondary ligands, have been reported¹². Ternary complexes of uranyl ion with 3,5-dinitrosalicylic acid and other carboxylic acids were also reported¹³. A considerable number of complexes of UO_2^{2+} -

carboxylate with aminoacids^{14,15} have been reported but there are only few reports^{16,17} on UO_2 -dicarboxylate with other dicarboxylic acids. Oxalate ion is also used for the separation of Pu(IV) and Th(IV) from U(VI) by precipitation¹⁸.

Since fatty acids are useful reagents for the extraction of uranyl ion, a study on the stabilities of uranyl complexes with dicarboxylic acids, assumes significance. Hence, protonation¹⁹ and uranyl complex equilibria of malonic²⁰ and oxalic acids²¹ have been studied. In the present paper the stability of ternary complexes has been reported. In these studies micellar medium is chosen for two reasons. 1) micelles decrease the dielectric constant of the medium, which is essential in the extraction of uranium and 2) micelles mimic the biological membrane and compartmentalize the chemical reactions.

Materials and Method

Solutions of uranyl nitrate, oxalic acid and malonic acid were prepared by dissolving G R grade (E. Merck, Germany) samples in triple distilled water. Aqueous solutions of AR grade sodium laurylsulphate (SLS) (Qualigen), cetyltrimethylammonium bromide (CTAB) (BDH) and TritonX-100 (TX) (E. Merck) were also prepared in triple distilled water. Alkalimetric titrations were carried out in the medium containing varying compositions of SLS (0.5 - 2.0%w/v), CTAB (0.5 - 2.5%w/v) and TX (0.5 - 2.5%v/v) maintaining an ionic strength of 0.17 mol dm⁻³ with sodium chloride at $303.0 \pm 0.1\text{K}$ temperature using constant temperature bath. Systronics (model 335) pH meter was used to monitor changes in hydrogen ion concentration. The glass electrode was equilibrated in a well stirred micellar solution containing inert electrolyte. The effect of variations in asymmetry, liquid junction potential, activity coefficient, sodium ion error and/or dissolved carbon dioxide on the response of glass electrode was taken into account in the form of correction factor ($\log F$). The $\log F$ was computed from the simulated acid-base titration data (PHCi) by SCPHD program²² for each of the solvent compositions. Its value was used to convert pH meter dial reading into logarithm of reciprocal of hydrogen ion concentration (pHEi) according to the eqn.(1).

$$\log F = \text{PHCi} - \text{PHEi} \quad (1)$$

Strong acid was titrated with alkali at regular intervals to check equilibration of the glass electrode. The calomel electrode was refilled with micellar solution (only TX and CTAB but not SLS since it forms precipitate with KCl) of equivalent composition as that of the titrand. In each titration, the titrand consists of approximately 1 mmol

mineral acid (HClO_4 in case of SLS and TX and HCl in case of CTAB because CTAB forms precipitate with HClO_4) in a total volume of 50cm^3 . Titrations of solutions containing different ratios (1:2.4 and 1:4.2) of metal to oxalic acid to malonic acid were carried out with 0.2 mol dm^{-3} sodium hydroxide.

Modelling strategy

A chemical model for complex equilibria consists of stoichiometric coefficients and logarithm of stability constants. The best-fit chemical models were arrived at by adopting a modelling strategy²³. Various models were obtained from the experimental data using MINIQUAD75²⁴. Some heuristics were followed²³ in the refinement of the stability constants. The best model among them was chosen based on statistical parameters.

Results and Discussion

Complex equilibria

The coordination number of uranyl ion is six²⁵ and three bidentate ligands are sufficient to satisfy the coordination number of the metal ion. Hence, the total number of primary and secondary ligands together is restricted to a maximum of three in generating the possible ternary species for modelling. Several thumb rules based on chemical principles and well established practices in multiple linear regression analysis²³ were followed in the refinement process which have resulted in the final model consisting of the species $\text{MLX}_2\text{H}^{2-}$, MLXH_2 and $\text{ML}_2\text{XH}^{3-}$. The best fit model was chosen as that with the lowest standard deviation (SD) in formation constants and minimum U_{corr} (corrected for degrees of freedom) which was corroborated by other statistical parameters²⁶ like χ^2 , crystallographic R etc., which are given in Table 1. The values of skewness between -0.06 and 0.91 evince that the residuals form a part of normal distribution. Kurtosis is the degree of peakedness of a distribution, usually taken relative to a normal distribution. If this value is equal to 3, the distribution of residuals is normal (mesokurtic) i.e. not very peaked or flat-topped. A high value indicates that the distribution is peaked (leptokurtic) and a low value represents a flat topped distribution called platykurtic.

The effects of errors in the influential parameters²³ like the concentration of ingredients on the stability constants were studied by incorporating errors in them in the range -1 to + 1 %. The results show that the order of affecting the magnitudes of stability constants is due to errors in the concentrations of alkali > acid > ligand2 > ligand1 > metal. The increased SD in stability constants on the introduction of errors confirms the correctness of the proposed models.

Table I— Best fit chemical models of mixed-ligand complexes of Uranium(VI) with oxalic and malonic acids in water-surfactant mixtures

Temp = 303K

 $\mu = 0.17 \text{ mol dm}^{-3}$

pH range = 2.0-6.0

% surfactant	log β_{mlxh} (SD)								
	MLX ₂ H ₂	MLXH ₂	ML ₂ XH	NP	U _{corr}	χ^2	R	Skewness	Kurtosis
0.0	23.44(8)	20.04(1)	18.06(1)	93	6.85	20.37	0.0114	-0.06	3.15
SLS(%w/v)									
0.5	22.17(2)	19.11(2)	17.30(5)	94	13.17	26.82	0.0152	0.39	2.81
1.0	23.05(1)	20.29(1)	18.16(3)	88	9.91	14.55	0.0135	0.42	2.83
1.5	24.33(1)	20.35(7)	20.12(2)	82	2.28	2.29	0.0066	-0.15	2.90
2.0	23.66(2)	20.79(2)	19.21(3)	76	5.96	29.16	0.0109	-0.10	5.06
TX(%v/v)									
0.5	24.54(8)	20.50(9)	20.06(1)	94	1.39	16.63	0.0059	-0.15	3.14
1.0	23.40(5)	21.69(3)	19.12(6)	93	32.37	51.67	0.0249	0.91	3.44
1.5	22.70(1)	19.73(1)	18.06(2)	94	13.74	70.21	0.0171	0.59	3.02
2.0	22.29(1)	19.76(1)	17.58(2)	91	12.16	70.02	0.0168	0.79	3.42
2.5	23.42(2)	20.42(2)	18.50(4)	95	11.96	48.93	0.0157	0.57	2.89
CTAB(%w/v)									
0.5	23.18(1)	20.33(2)	18.19(4)	93	13.44	47.31	0.0172	0.69	3.24
1.0	23.71(2)	20.77(2)	18.76(5)	90	10.57	37.96	0.0156	0.63	3.13
1.5	24.29(7)	20.33(8)	19.15(3)	90	1.85	23.56	0.0066	-0.35	4.19
2.0	22.74(1)	20.08(2)	17.92(4)	95	27.28	96.84	0.0239	0.86	3.72
2.5	23.65(2)	19.80(2)	18.46(7)	91	3.23	16.92	0.0085	-0.43	4.33

Distribution diagrams

The concentrations of binary metal-ligand complexes were found to be less than 10% in the presence of ternary complexes. Hence they are not presented in the distribution diagrams (Fig. 1). Since ternary complexes are more stable than binary complexes, the latter are converted to the ternary complexes in the presence of secondary ligand. The change in the stability of ternary complexes as compared to their binary analogues was quantified^{27,28}.

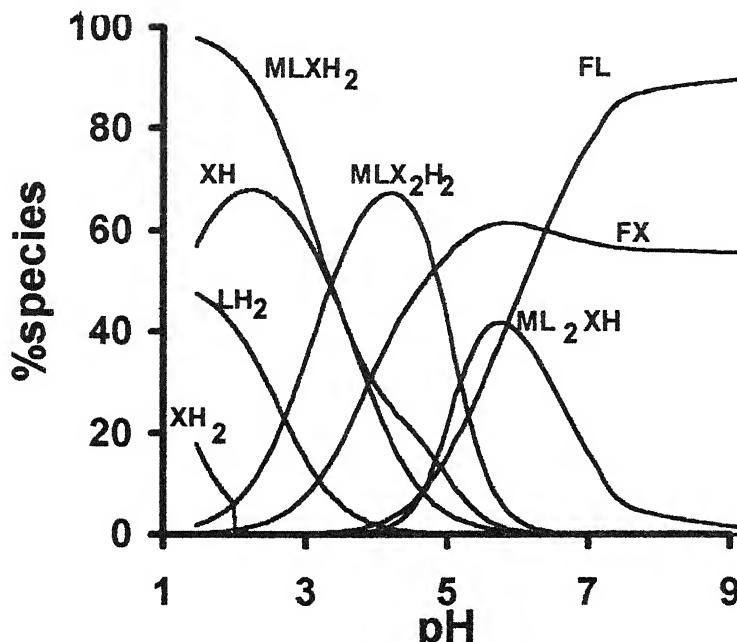
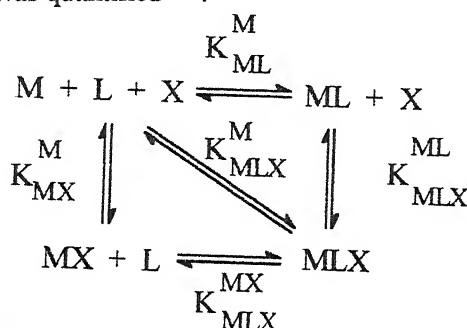


Fig. 1—Distribution diagrams of various mixed ligand species. FL, FX · concentrations of protonated primary and secondary ligands, respectively

In one of the approaches the difference in stability ($\Delta\log K$) for the two reactions *viz.* ML with X and M(aq) with L and X (where X is a secondary ligand) is compared with that calculated purely on statistical grounds (eqn 2)

$$\Delta\log K = \log K_{MLX}^{ML} - \log K_{MX}^M = \log K_{MLX}^{MX} - \log K_{ML}^M \quad (2)$$

Both electrostatic theories of binary complex formation and statistical arguments suggest that more coordination positions of a given multivalent hydrated metal ion will be available for the first ligand than for the second. Hence, the usual order of stability $K_{ML}^M > K_{ML2}^{ML}$ holds good. This leads to a negative value for $\Delta\log K$. The statistical values of $\Delta\log K$ for bidentate L and X are -0.4, -0.6 and between -0.9 and -0.3 for octahedral, square planar and distorted octahedral complexes, respectively. Whenever the experimental value of $\Delta\log K$ exceeds the statistical value, it can be inferred that the ternary complex is formed as a result of interaction of MLH_h with MXH_h . Negative values of $\Delta\log K$ can be understood as the secondary ligand forms a more stable complex with hydrated metal ion than with ML, which does not mean that the ternary complex is absent. The ternary complexes with N,N donor primary ligands are observed²⁹⁻³³ to have positive $\Delta\log K$ values if the secondary ligands are O, O⁻ donors, negative if the secondary ligands are N,N donors and midway between the two if the secondary ligands are N,O donors.

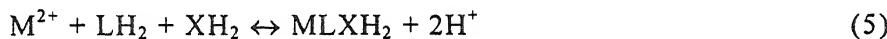
Another approach to quantify the stability of ternary complexes was based on the disproportionation constant ($\log X$) given by eqn. 3, which corresponds to the equilibrium given by eqn. 4. Under these equilibrium conditions, one would expect 50% ternary complex and 25% each of the binary complexes to be formed and the value³⁴⁻³⁶ of $\log X$ to be 0.6. Any value greater than 0.6 accounts for the extra stability of MLX , which results from several factors like charge neutralization, chelate ring size, stacking interactions, hydrogen bonding and charge transfer interactions.

$$\log X = 2\log K_{MLX}^{ML} - \log K_{MX_2}^M - \log K_{ML}^M \quad (3)$$

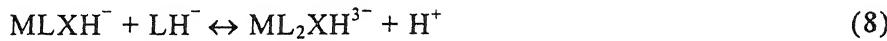


The values of $\Delta\log K$ and $\log X$ could not be calculated for the present systems, using the transformations given in Table 2 due to the absence of the relevant binary complexes

A perusal of Fig. 1 reveals that at very low pH the concentrations of $MLX_2H_2^{2-}$ and ML_2XH^{3-} complexes are less than those of protonated ligands. As the pH increases the concentrations of $MLX_2H_2^{2-}$ and ML_2XH^{3-} go through maximum but the concentration of $MLXH_2$ species is high at lower pH and gradually decreases as the pH increases. In the pH region 1.5-3.5 oxalic and malonic acids exist as LH (HC_2O_4) and XH_2 ($H_4C_3O_4$) respectively¹⁹. These protonated ligands interact with the metal ion to form $MLXH_2$. Since the pK_a values of oxalic acid are lower than those of malonic acid, oxalic acid is readily deprotonated. Hence the proton in protonated ternary complexes must be present on malonate but not on oxalate. The possible formation of other ternary species is shown in the following equilibria.



(or)



(or)



The possible structures of these ternary complexes are given in Fig. 2. The structures of the complexes are proposed based on the literature and chemical principles. Literature also shows that the coordination number of uranyl ion is 6 and oxalate and malonate act as bidentate ligands. It also shows that water occupies one of the coordination positions.

The magnitudes of protonation constants of malonic acid are higher than those of oxalic acid¹⁹. Therefore, mono- or di- protonated malonate ion exists in the pH range where deprotonated oxalate ion can exist. For example, $MLXH_2$ (L = oxalate), (X =malonate) can be represented as $M(LH_2)(X)$, $ML(XH_2)$ or $M(LH)(XH)$ and the possibility of $M(LH_2)(X)$ can be ruled out because oxalic acid cannot exist in the protonated form when malonic acid is present as deprotonated ligand. The possibility of $ML(XH_2)$ can also be ruled out since diprotonated ligand (XH_2) cannot form the complex due to unavailability of coordinating atoms. Hence, the $MLXH_2$ species must be present as $M(LH)(XH)$. Monoprotonated oxalic or malonic acid shall always act as monodentate ligand due to the availability of one coordinating atom. Thus the structure of $MLXH_2$ shall be as represented in Fig. 2.

Similarly $[MLX_2H_2]^{2-}$ can be represented as $[ML(XH)_2]^{2-}$ and $[ML_2XH]^{3-}$ as $[ML_2(XH)]^{3-}$ whose structures are also shown in Fig. 2.

Table 2- Calculation of $\Delta\log K$ and $\log X$ from overall stability constants

$\Delta\log K_{1112} = \log\beta_{1112} - \log\beta_{1102} - \log\beta_{1010}$	$\log X_{1112} = 2 \log\beta_{1112} - \log\beta_{1204} - \log\beta_{1020}$
$= \log\beta_{1112} - \log\beta_{1101} - \log\beta_{1011}$	$= 2 \log\beta_{1112} - \log\beta_{1203} - \log\beta_{1021}$
$= \log\beta_{1112} - \log\beta_{1100} - \log\beta_{1012}$	$= 2 \log\beta_{1112} - \log\beta_{1202} - \log\beta_{1022}$
	$= 2 \log\beta_{1112} - \log\beta_{1201} - \log\beta_{1023}$
	$= 2 \log\beta_{1112} - \log\beta_{1200} - \log\beta_{1024}$
$\Delta\log K_{1122} = \log\beta_{1122} - \log\beta_{1102} - \log\beta_{1020}$	$\log X_{1122} = 2 \log\beta_{1122} - \log\beta_{1204} - \log\beta_{1040}$
$= \log\beta_{1122} - \log\beta_{1101} - \log\beta_{1021}$	$= 2 \log\beta_{1122} - \log\beta_{1203} - \log\beta_{1041}$
$= \log\beta_{1122} - \log\beta_{1100} - \log\beta_{1022}$	$= 2 \log\beta_{1122} - \log\beta_{1202} - \log\beta_{1042}$
	$= 2 \log\beta_{1122} - \log\beta_{1201} - \log\beta_{1043}$
	$= 2 \log\beta_{1122} - \log\beta_{1200} - \log\beta_{1044}$
$\Delta\log K_{1211} = \log\beta_{1211} - \log\beta_{1201} - \log\beta_{1010}$	$\log X_{1211} = 2 \log\beta_{1211} - \log\beta_{1401} - \log\beta_{1021}$
$= \log\beta_{1211} - \log\beta_{1200} - \log\beta_{1011}$	$= 2 \log\beta_{1211} - \log\beta_{1400} - \log\beta_{1022}$

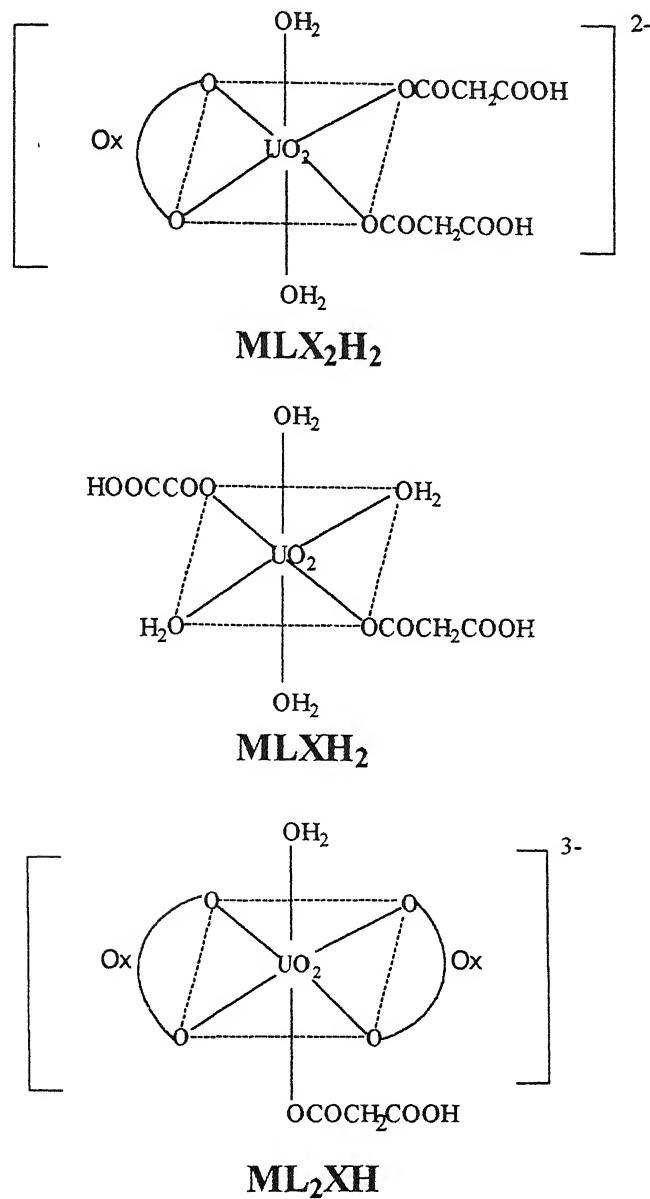


Fig. 2—Probable structures of uranyl-oxalate-malonate chelates .

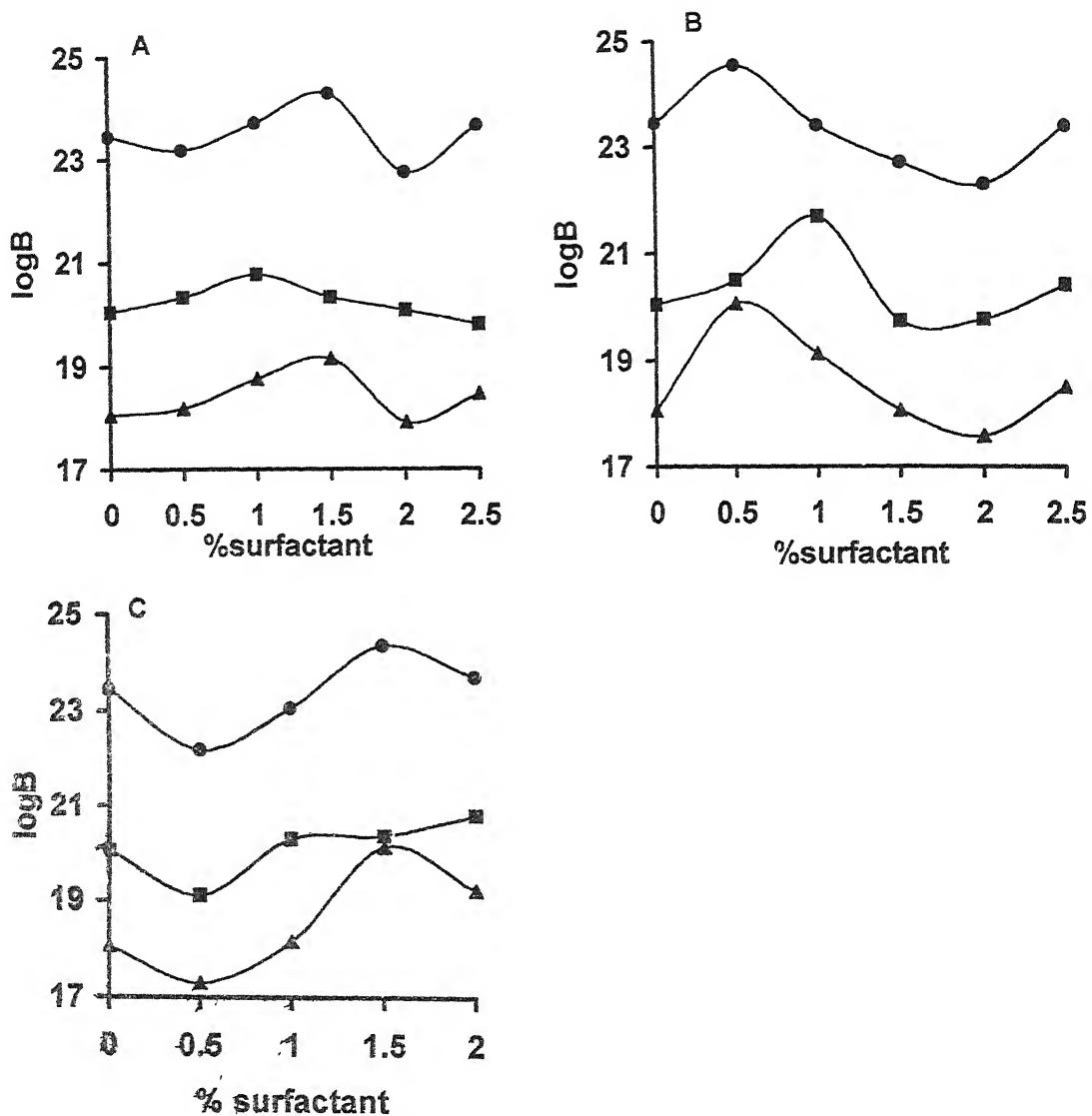


Fig. 3 – Variation of formation constant ($\log \beta_{mbh}$) with percentage concentration of surfactant.

(A) CTAB, (B) TX and (C) SLS. ●MLX₂H₂ ■MLXH₂ ▼ML₂XH

Effect of micelles

The variation of stability constants ($\log\beta$) with percentage of surfactant is shown in Fig 3. Similar to binary complexes^{19,20}, the stabilities of ternary complexes also exhibit nonlinear trend. This is also reflected in the maximum concentration of the species and the pH at maximum percentage concentration of the species (Table 3). The dielectric constant of the medium decreases^{37,38} with increasing concentration of the surfactant. The variation in the stability of the charged complex species depends on the polarity of the medium, charge on the micellar surface (Stern layer), and on electrostatic attraction or repulsive forces operating between the complex species and the micellar surface. The species $[MLX_2H_2]^{2-}$ and $[ML_2XH]^{3-}$ should be stabilised by CTAB due to electrostatic interactions but they should be destabilised due to the decreased dielectric constant. The magnitudes of these opposing factors determine the trend in variation of stability constant with increase in CTAB content as shown in Fig 3A. The stability of $MLXH_2$ is little affected by the medium because it is a neutral species. Due to similar reasons the stability of the ternary complexes varies nonlinearly with the increased SLS content (Fig. 3C). As TX is a neutral surfactant, the stabilities are decreased due to the decreased (Fig 3B) dielectric constant and decreased electrostatic interactions.

Table 3— Effect of surfactant on the pH at which maximum concentration of the species is observed for the ternary complexes of uranium(VI) with oxalic and malonic acids

Surfactant	pH(%concentration of species)		
	MLX_2H_2	$MLXH_2$	ML_2XH
0.0	3.59(83.1)	2.0(73.3)	5.39(26.4)
CTAB(%w/v)			
0.5	4.33(73.1)	2.0(83.3)	5.72(25.1)
1.0	4.33(75.3)	2.0(83.8)	5.79(27.8)
1.5	4.45(78.9)	2.0(84.1)	5.69(28.9)
2.0	4.43(64.9)	2.3(82.1)	5.57(23.9)
2.5	3.47(93.1)	2.0(67.4)	5.56(14.1)

Table 3 Contd...

Table 3 Contd

TX(%v/v)			
0.5	3.53(94.1)	2.0(56.8)	5.83(46.6)
1.0	4.63(92.8)	2.93(98.2)	5.95(41.7)
1.5	4.35(75.4)	2.08(83.6)	5.65(34.1)
2.0	4.34(60.9)	2.11(86.7)	5.57(27.2)
2.5	4.35(75.9)	2.03(83.9)	5.74(29.5)
SLS(%w/v)			
0.5	4.21 (78.4)	2.05(81.7)	5.70(25.5)
1.0	4.20(71.9)	2.10(83.3)	5.71(22.0)
1.5	4.10(95.1)	2.21(84.2)	5.33(37.1)
2.0	4.50(80.2)	2.02(97.7)	6.00(26.2)

Conclusions

- (1) The interaction of oxalic and malonic acids with uranyl ion in the pH range 2-6 forms $[\text{UO}_2(\text{C}_2\text{O}_4)(\text{H}_3\text{C}_3\text{O}_4)_2]^2-$, $[\text{UO}_2(\text{HC}_2\text{O}_4)(\text{H}_3\text{C}_3\text{O}_4)]$ and $[\text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_3\text{C}_3\text{O}_4)]^{3-}$ species.
- (2) The concentrations of binary complexes of uranium with oxalic or malonic acid are very small (less than 10%) compared to those of the ternary complexes.
- (3) The magnitudes of stability constants of the ternary complexes exhibit non-linear trend with the concentrations of the surfactant. This trend is due to the decrease in the polarity of the solvent with increased surfactant concentration, which destabilizes the charged complex species. The second factor is the electrostatic interactions between the complex species and the charged Stern layer of the micelles.

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Semi-circle theorems for magnetorotatory double-diffusive convection (MRDDC) problems of Veronis and Stern types

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Abstract

The present paper derives semi-circle theorems, for magnetorotatory double-diffusive convection problems of Veronis and Stern types, that prescribe upper limits for the complex growth rate of oscillatory motions of neutral or growing amplitude in such a manner that it naturally culminates in sufficient conditions precluding the non-existence of such motions for an initially bottom heavy as well as an initially top heavy configurations. Further, results for double-diffusive convection problems with or without the individual effects of a rotation or a magnetic field follow as a consequence

(Keywords: magnetorotatory/double-diffusive/convection/oscillatory/growth rate)

Introduction

Double-diffusive convection, with its archetypal case of heat and salt, generally referred to as thermohaline convection, has been extensively studied in the recent past on account of its interesting complexities as well as its direct relevance in many problems of practical interest in the fields of the Limnology, Oceanography, Geophysics, Astrophysics and Chemical Engineering etc. For a broad and a recent view of the subject one may be referred to Brandt and Fernando¹. Two fundamental configurations have been studied in the context of thermohaline instability problem, the first one by Stern² wherein the temperature gradient is stabilizing and the concentration gradient is destabilizing and the second one by Veronis³ wherein the temperature gradient is destabilizing and the concentration gradient is stabilizing. The main results derived by Stern and Veronis for their respective configurations are that both allow the occurrence of a stationary pattern of motions or oscillatory motions of growing amplitude provided the destabilizing concentration gradient or the temperature gradient is sufficiently large. However, stationary pattern of motion is the

preferred mode of setting in of instability in case of Stern's configuration whereas oscillatory motions of growing amplitude are preferred in Veronis' configuration. Further, these results are independent of the initially gravitationally stable or unstable character of the two configurations. It is important to note that Veronis' work is restricted to dynamically free boundaries whereas Stern's work assumes the 'principle of exchange of stabilities'. Keeping in view the foregoing discussion, thermohaline configurations of Veronis and Stern types can therefore be further classified into the following two classes:

- (i) The first class in which thermohaline instability manifests itself when the total density field is initially bottom heavy and
- (ii) The second class in which thermohaline instability manifests itself when the total density field is initially top heavy.

Banerjee and co-authors^{4,5} have derived a characterization theorem for rotatory (hydromagnetic) double-diffusive problem of Veronis' type that disproves the existence of oscillatory motion of growing amplitude in an initially bottom heavy configuration if (i) $\tau \leq \sigma$ ($\tau\sigma_1 \leq \sigma$) and (ii) $\mathfrak{R}_s \leq \frac{27\pi^4}{4} \left(1 + \frac{\tau}{\sigma}\right)$, where τ , σ , σ_1 and \mathfrak{R}_s , respectively denote the Lewis number, the thermal Prandtl number, the magnetic Prandtl number and the concentration Rayleigh number. The restriction (i) in the above results of Banerjee and co-authors may be physically justifiable in certain situations, however, it is not mathematically palpable. Further, the sufficient character of condition (ii) coupled with the nature of their mathematical analysis strongly suggest the possibility of the derivation of an upper bound for the modulus of the complex growth rate of an arbitrary oscillatory perturbation which may be neutral or unstable that will automatically take care of condition (ii) and yield the results of Banerjee and co-authors without the restriction (i) and will also be uniformly applicable for initially bottom heavy as well as initially top heavy configurations.

Motivated by these considerations, the present paper purports to deal with the more general magnetorotatory double-diffusive convection problems of Veronis' and Stern's types and derives semi-circle theorems that prescribe upper limits for the complex growth rate of oscillatory motions of neutral or growing amplitude in such a manner that it naturally culminates in sufficient conditions precluding the non-existence of such motions for initially bottom heavy as well as initially top heavy

configurations. Further, results for simple double-diffusive problems with or without the individual effects of a rotation or a magnetic field follow as a consequence.

Basic Equations and Boundary Conditions

Following the usual steps of linear stability theory the non-dimensional linearized perturbation equations governing the magnetorotatory double-diffusive convection problem with a uniform rotation and a uniform magnetic field both acting in the vertical direction opposite to the force field of gravity are given by (c f. Veronis³ and Chandrasekhar⁶).

$$(D^2 - a^2) \left(D^2 - a^2 - \frac{p}{\sigma} \right) w = \mathfrak{R} a^2 \theta - \mathfrak{R}_s a^2 \phi - QD(D^2 - a^2) h_z + TD\zeta \quad (1)$$

$$(D^2 - a^2 - p) \theta = -w \quad (2)$$

$$\left(D^2 - a^2 - \frac{p}{\tau} \right) \phi = -\frac{w}{\tau} \quad (3)$$

$$\left(D^2 - a^2 - \frac{p\sigma_1}{\sigma} \right) h_z = -Dw \quad (4)$$

$$\left(D^2 - a^2 - \frac{p}{\sigma} \right) \zeta = -QD\xi - Dw \quad (5)$$

$$\left(D^2 - a^2 - \frac{p\sigma_1}{\sigma} \right) \xi = -D\zeta \quad (6)$$

together with the boundary conditions

$$w = 0 = \theta = \phi = Dw = h_z = \zeta = D\xi \text{ at } z = 0 \text{ and } z = 1 \quad (7)$$

(both boundaries rigid and perfectly conducting)

In the above equations, z is the real independent variable such that $0 \leq z \leq 1$, $D = d/dz$ is the differentiation with respect to z ; a^2 , σ , τ and σ_1 are positive constants; Q and T are non-negative constants; \mathfrak{R} and \mathfrak{R}_s are also constants that could be positive or negative; $p = p_r + ip_i$ is a complex constant in general and the dependent variables w , θ , ϕ , h_z , ζ and ξ are complex-valued functions of the real variable z . The meaning of the symbols from the physical point of view are as follows: z is the vertical co-ordinate, d/dz is the differentiation along the vertical direction; a^2 is the square of the wave number; σ is the thermal Prandtl number; τ is the Lewis number, σ_1 is the magnetic Prandtl number, \mathfrak{R} is the thermal Rayleigh number; \mathfrak{R}_s is the concentration Rayleigh number, Q is the Chandrasekhar number; T is the Taylor number; p is the complex growth rate, w , h_z , ζ and ξ are the vertical components of velocity, magnetic field, vorticity and current density respectively; θ is the temperature and ϕ is the concentration.

Mathematical Analysis

System of eqn. (1) – (6) together with the boundary conditions (7) constitute an eigenvalue problem for the complex growth rate $p = p_r + ip_i$, for given values of the other parameters, namely, a^2 , σ , \mathfrak{R} , \mathfrak{R}_s , Q , T , σ_1 and τ and a given state of the system is stable, neutral or unstable according as p_i is negative, zero or positive. Further,

- (a) $p_r \neq 0$ and $p_r \geq 0$ describe oscillatory motions of neutral or growing amplitude;
- (b) $\mathfrak{R} > 0$ and $\mathfrak{R}_s > 0$ and either $Q = 0 = T$ or $Q = 0$ or $T = 0$ respectively describe Veronis' thermohaline configuration (VTC) or rotatory VTC or hydromagnetic VTC;
- (c) $\mathfrak{R} < 0$ and $\mathfrak{R}_s < 0$ and either $Q = 0 = T$ or $Q = 0$ or $T = 0$ respectively describe Stern's thermohaline configuration (STC) or rotatory STC or hydromagnetic STC;
- (d) $\lambda = \frac{\mathfrak{R}}{\mathfrak{R}_s} \leq 1$ $\left(\hat{\lambda} = \frac{|\mathfrak{R}_s|}{|\mathfrak{R}|} \leq 1 \right)$ describes an initially bottom heavy VTC (STC);
and
- (e) $\lambda \geq 1$ $\left(\hat{\lambda} \geq 1 \right)$ describes an initially top heavy VTC (STC).

Finally, if $p_r = 0 \Rightarrow p_i = 0, \forall \alpha^2$, then the principle of exchange of stabilities is valid, otherwise we have over stability at least when instability sets in as certain modes.

We prove the following Theorems :

Theorem 1 (A Semi-Circle Theorem for Magnetorotatory VTC)

If $(p, w, \theta, \phi, h_z, \zeta, \xi)$, $p = p_r + ip_i$, $p_r \geq 0, p_i \neq 0$, is a nontrivial solution of the eqn. (1) – (6) together with the boundary conditions (7), and $\Re > 0, \Re_s > 0, Q \geq 0$ and $T \geq 0$, then

$$|p| < \frac{\lambda \Re_s}{4\pi^2(1+\delta)} \sqrt{\Omega^2 - 1}$$

$$\text{where } \frac{4\lambda \Re_s}{27\pi^4(1+\delta)}, \delta = \min \left\{ \frac{\tau}{\sigma}, \frac{1}{\sigma_1}, 1 \right\} \text{ and } \lambda = \frac{\Re}{\Re_s}.$$

Proof. Multiplying (1) by w^* (w^* is the complex conjugate of w) throughout, integrating the resulting equation over the vertical range of z and utilizing (2) – (6), we get

$$\begin{aligned} & \int_0^1 w^* (D^2 - \alpha^2) \left(D^2 - \alpha^2 - \frac{p}{\sigma} \right) w \, dz + \Re \alpha^2 \int_0^1 \theta (D^2 - \alpha^2 - p^*) \theta^* \, dz \\ & - \tau \Re_s \alpha^2 \int_0^1 \phi \left(D^2 - \alpha^2 - \frac{p^*}{\tau} \right) \phi^* \, dz + Q \int_0^1 (D^2 - \alpha^2) h_z \left(D^2 - \alpha^2 - \frac{p^* \sigma_1}{\sigma} \right) h_z^* \, dz \\ & - T \int_0^1 \zeta \left(D^2 - \alpha^2 - \frac{p^*}{\sigma} \right) \zeta^* \, dz - QT \int_0^1 \xi^* \left(D^2 - \alpha^2 - \frac{p \sigma_1}{\sigma} \right) \xi \, dz = 0. \end{aligned} \quad (8)$$

Subsequently, for convenience, we will omit the limits of integration from the integral sign and dz from the integrand.

Integrating the various terms of (8) by parts for an appropriate number of times and using the boundary conditions (7), we get

$$\begin{aligned}
 & \int \left((D^2 - \alpha^2) w \right)^2 + \frac{p}{\sigma} \int \left[|Dw|^2 + \alpha^2 |w|^2 \right] + \tau \Re_s \alpha^2 \int \left(|D\phi|^2 + \alpha^2 |\phi|^2 \right) \\
 & + Q \int \left((D^2 - \alpha^2) h_z \right)^2 + QT \int \left[|D\xi|^2 + \alpha^2 |\xi|^2 \right] + T \int \left[|D\zeta|^2 + \alpha^2 |\zeta|^2 \right] \\
 & - \Re \alpha^2 \int \left[|D\theta|^2 + \alpha^2 |\theta|^2 \right] + \Re_s \alpha^2 p^* \int |\phi|^2 + \frac{Qp^* \sigma_1}{\sigma} \int \left[|Dh_z|^2 + \alpha^2 |h_z|^2 \right] \\
 & - \Re \alpha^2 p^* \int |\theta|^2 + \frac{Tp^*}{\sigma} |\zeta|^2 + \frac{QT\sigma_1 p}{\sigma} \int |\xi|^2 = 0. \tag{9}
 \end{aligned}$$

Equating the real and imaginary parts of (9) to zero and canceling p , ($\neq 0$) throughout from the imaginary part, we have

$$\begin{aligned}
 & \int \left((D^2 - \alpha^2) w \right)^2 + \frac{p_r}{\sigma} \int \left[|Dw|^2 + \alpha^2 |w|^2 \right] + \tau \Re_s \alpha^2 \int \left(|D\phi|^2 + \alpha^2 |\phi|^2 \right) \\
 & + Q \int \left((D^2 - \alpha^2) h_z \right)^2 + QT \int \left[|D\xi|^2 + \alpha^2 |\xi|^2 \right] + T \int \left[|D\zeta|^2 + \alpha^2 |\zeta|^2 \right] \\
 & - \Re \alpha^2 \int \left[|D\theta|^2 + \alpha^2 |\theta|^2 \right] + p_r \left[\Re_s \alpha^2 \int |\phi|^2 + \frac{Q\sigma_1}{\sigma} \int \left[|Dh_z|^2 + \alpha^2 |h_z|^2 \right] \right. \\
 & \left. - \Re \alpha^2 \int |\theta|^2 + \frac{T}{\sigma} \int |\zeta|^2 + \frac{QT\sigma_1}{\sigma} \int |\xi|^2 \right] = 0 \tag{10}
 \end{aligned}$$

and

$$\begin{aligned} & \frac{1}{\sigma} \int [|Dw|^2 + \alpha^2 |w|^2] - \Re_s \alpha^2 \int |\phi|^2 - \frac{Q\sigma_1}{\sigma} \int [|Dh_z|^2 + \alpha^2 |h_z|^2] \\ & + \Re \alpha^2 |\theta|^2 - \frac{T}{\sigma} \int |\zeta|^2 + \frac{QT\sigma_1}{\sigma} \int |\xi|^2 = 0. \end{aligned} \quad (11)$$

Multiplying (11) by p_r and adding the resulting equation to (10), we have

$$\begin{aligned} & \int [(D^2 - \alpha^2) w]^2 + \frac{2p_r}{\sigma} \left[\int [|Dw|^2 + \alpha^2 |w|^2] + QT\sigma_1 \int |\xi|^2 \right] \\ & + \tau R_s \alpha^2 \int [|D\phi|^2 + \alpha^2 |\phi|^2] + Q \int [(D^2 - \alpha^2) h_z]^2 + QT \int [|D\xi|^2 + \alpha^2 |\xi|^2] \\ & + T \int [|D\zeta|^2 + \alpha^2 |\zeta|^2] - \Re \alpha^2 \int [|D\theta|^2 + \alpha^2 |\theta|^2] = 0. \end{aligned} \quad (12)$$

Since, w , θ , ϕ , h_z and ζ vanish at $z = 0$ and $z = 1$, therefore Rayleigh-Ritz inequality⁷ yields

$$\left. \begin{aligned} \text{(i)} \quad & \int |Dw|^2 \geq \pi^2 \int |w|^2 \\ \text{(ii)} \quad & \int |D\theta|^2 \geq \pi^2 \int |\theta|^2 \\ \text{(iii)} \quad & \int |D\phi|^2 \geq \pi^2 \int |\phi|^2 \\ \text{(iv)} \quad & \int |Dh_z|^2 \geq \pi^2 \int |h_z|^2 \\ \text{(v)} \quad & \int |D\zeta|^2 \geq \pi^2 \int |\zeta|^2 \end{aligned} \right] \quad (13)$$

Further, utilizing Schwartz inequality, we have

$$\begin{aligned}
\left(\int |w|^2 \right)^{\frac{1}{2}} \left(\int |D^2 w|^2 \right)^{\frac{1}{2}} &\geq \left| - \int w^* D^2 w \right| = \int |Dw|^2 \\
&\geq \pi^2 \int |w|^2 \quad [\text{Using (13(1))}]
\end{aligned}$$

Consequently,

$$\int |D^2 w|^2 \geq \pi^4 \int |w|^2 \quad (14)$$

This together with inequality (13(i)) gives

$$\int \left(|D^2 w|^2 + 2\alpha^2 |Dw|^2 + \alpha^4 |w|^2 \right) \geq (\pi^2 + \alpha^2)^2 \int |w|^2 \quad (15)$$

Further, (2) implies that

$$\begin{aligned}
\int |w|^2 &= \int w w^* = \int [(D^2 - \alpha^2)\theta - p\theta] [(D^2 - \alpha^2)\theta^* - p^* \theta^*] \\
&= \int |(D^2 - \alpha^2)\theta|^2 + 2p_r \int (|D\theta|^2 + \alpha^2 |\theta|^2) + |p|^2 \int |\theta|^2
\end{aligned} \quad (16)$$

Since, $p_r \geq 0$, therefore it follows from (16) that

$$\int |w|^2 \geq \int |(D^2 - \alpha^2)\theta|^2 + |p|^2 \int |\theta|^2 \quad (17)$$

and

$$\int |w|^2 > \int |(D^2 - \alpha^2)\theta|^2 \quad (18)$$

Also, emulating the derivation of inequality (14) and (15), we have

$$\int |(D^2 - a^2)\theta|^2 = \int \left(|D^2\theta|^2 + 2a^2|D\theta|^2 + a^4|\theta|^2 \right) \geq (\pi^2 + a^2)^2 \int |\theta|^2 \quad (19)$$

Combining inequalities (17) and (19), we have

$$\int |w|^2 \geq \left\{ (\pi^2 + a^2)^2 + |p|^2 \right\} \int |\theta|^2 \quad (20)$$

Again

$$\begin{aligned} \int |w|^2 &= \left(\int |w|^2 \right)^{\frac{1}{2}} \left(\int |w|^2 \right)^{\frac{1}{2}} \\ &> (\pi^2 + a^2) \left\{ 1 + \frac{|p|^2}{(\pi^2 + a^2)^2} \right\}^{\frac{1}{2}} \left(\int |(D^2 - a^2)\theta|^2 \right)^{\frac{1}{2}} \left(\int |\theta|^2 \right)^{\frac{1}{2}} \quad [\text{Using (18) and (20)}] \\ &\geq (\pi^2 + a^2) \left\{ 1 + \frac{|p|^2}{(\pi^2 + a^2)^2} \right\}^{\frac{1}{2}} \left| - \int \theta^* (D^2 - a^2)\theta \right| \quad [\text{Using Schwartz inequality}] \\ &= (\pi^2 + a^2) \left\{ 1 + \frac{|p|^2}{(\pi^2 + a^2)^2} \right\}^{\frac{1}{2}} \int (|D\theta|^2 + a^2|\theta|^2) \end{aligned} \quad (21)$$

Using inequality (15) in the first integral, inequalities (13) and (21) in (12) and utilizing the fact that $p_r \geq 0$, we get

$$\begin{aligned} &(\pi^2 + a^2)^2 \int |w|^2 + \tau \Re_s a^2 (\pi^2 + a^2) \int |\phi|^2 \\ &+ Q(\pi^2 + a^2) \int (|Dh_s|^2 + a^2|h_s|^2) + T(\pi^2 + a^2) \int |\zeta|^2 \end{aligned}$$

$$< \frac{\Re a^2}{(\pi^2 + a^2)} \left\{ 1 + \frac{|p|^2}{(\pi^2 + a^2)^2} \right\}^{-\frac{1}{2}} \int |w|^2 \quad (22)$$

Eqn (11) upon using [13(i)] yields the following inequalities

$$\Re_s a^2 \int |\phi|^2 > \frac{(\pi^2 + a^2)}{\sigma} \int |w|^2 - \frac{Q\sigma_1}{\sigma} \int [Dh_z|^2 + a^2|h_z|^2] - \frac{T}{\sigma} \int |\zeta|^2 \quad (23)$$

$$Q \int [Dh_z|^2 + a^2|h_z|^2] > \frac{(\pi^2 + a^2)}{\sigma} \int |w|^2 - \frac{\Re_s a^2 \sigma}{\sigma_1} \int |\phi|^2 - \frac{T}{\sigma} \int |\zeta|^2 \quad (24)$$

and

$$T|\zeta|^2 > (\pi^2 + a^2) \int |w|^2 - Q\sigma_1 \int [Dh_z|^2 + a^2|h_z|^2] - \Re_s a^2 \sigma \int |\phi|^2 \quad (25)$$

Inequality (22) coupled with each of the inequalities (23)–(25) yields the following inequalities respectively :

$$\begin{aligned} & (\pi^2 + a^2)^2 \left(1 + \frac{\tau}{\sigma} \right) \int |w|^2 + Q(\pi^2 + a^2) \left(1 - \frac{\tau\sigma_1}{\sigma} \right) \int [Dh_z|^2 + a^2|h_z|^2] \\ & + T(\pi^2 + a^2) \left(1 - \frac{\tau}{\sigma} \right) \int |\zeta|^2 < \frac{\Re_s a^2}{(\pi^2 + a^2)} \left\{ 1 + \frac{|p|^2}{(\pi^2 + a^2)^2} \right\}^{-\frac{1}{2}} \int |w|^2 \end{aligned} \quad (26)$$

$$\begin{aligned} & (\pi^2 + a^2)^2 \left(1 + \frac{1}{\sigma_1} \right) \int |w|^2 + \Re_s a^2 (\pi^2 + a^2) \left\{ \tau - \frac{\sigma}{\sigma_1} \right\} \int |\phi|^2 \\ & + T(\pi^2 + a^2) \left(1 - \frac{1}{\sigma_1} \right) \int |\zeta|^2 < \frac{\Re a^2}{(\pi^2 + a^2)} \left\{ 1 + \frac{|p|^2}{(\pi^2 + a^2)^2} \right\}^{-\frac{1}{2}} \int |w|^2 \end{aligned} \quad (27)$$

and

$$2(\pi^2 + a^2)^2 \int |w|^2 + Q(\pi^2 + a^2) \{1 - \sigma_1\} \int (|Dh_z|^2 + a^2 |h_z|^2) \\ + \Re_s a^2 (\pi^2 + a^2) \{\tau - \sigma\} \int |\phi|^2 < \frac{\Re a^2}{(\pi^2 + a^2)} \left\{ 1 + \frac{|p|^2}{(\pi^2 + a^2)^2} \right\}^{-\frac{1}{2}} \int |w|^2 \quad (28)$$

Now, if $\delta = \min\left(\frac{\tau}{\sigma}, \frac{1}{\sigma_1}, 1\right)$, then depending on the value of δ , exactly one of the inequalities (26)–(28) will imply that

$$(1 + \delta)(\pi^2 + a^2)^2 \int |w|^2 < \frac{\Re a^2}{(\pi^2 + a^2)} \left\{ 1 + \frac{|p|^2}{(\pi^2 + a^2)^2} \right\}^{-\frac{1}{2}} \int |w|^2 \quad (29)$$

Since the minimum value of $\frac{(\pi^2 + a^2)^3}{a^2}$ with respect to a^2 is $\frac{27\pi^4}{4}$, it therefore follows from inequality (29) that

$$\frac{27\pi^4}{4} (1 + \delta) \left\{ 1 + \frac{|p|^2}{(\pi^2 + a^2)^2} \right\}^{-\frac{1}{2}} < \Re = \lambda \Re_s \quad (30)$$

Inequality (30) implies that

$$|p| < (\pi^2 + a^2) \sqrt{\Omega^2 - 1} \quad (31)$$

where $\Omega = \frac{4\lambda \Re_s}{27\pi^4(1 + \delta)} \left(= \frac{4\Re}{27\pi^4(1 + \delta)} \right)$

Further, it follows from inequality (29) that

$$\frac{(\pi^2 + a^2)(\pi^2 + a^2)^2 (1 + \delta)}{a^2} < \mathfrak{R}_s \lambda \quad (32)$$

Since the minimum value of $\frac{(\pi^2 + a^2)^2}{a^2}$ with respect of a^2 is $4\pi^2$, therefore it follows from inequality (32) that

$$(\pi^2 + a^2) < \frac{\lambda \mathfrak{R}_s}{4\pi^2(1 + \delta)} \quad (33)$$

Combining inequalities (31) & (33), we get

$$|P| < \frac{\lambda \mathfrak{R}_s}{4\pi^2(1 + \delta)} \sqrt{\Omega^2 - 1}.$$

This completes the proof of the theorem.

Theorem 1, from the point of view of hydrodynamic stability theory, may be stated as : the complex growth rate $p = p_r + ip_i$ of an arbitrary oscillatory perturbation of neutral or growing amplitude in magnetorotatory double-diffusive instability of Veronis type lies inside a semicircle in the right half of the $p_r p_i$ -plane whose centre is at the origin and whose radius is $\frac{\lambda \mathfrak{R}_s}{4\pi^2(1 + \delta)} \sqrt{\Omega^2 - 1} = \frac{\mathfrak{R}}{4\pi^2(1 + \delta)} \sqrt{\Omega^2 - 1}$. This result is uniformly valid for an initially top heavy as well as an initially bottom heavy configuration.

Corollary 1 : If, $(p, w, \theta, \phi, h_z, \zeta, \xi) p = p_r + ip_i, p_i \neq 0$, is a nontrivial solution of eqn. (1) – (6) together with the boundary conditions (7) and $\mathfrak{R} > 0, \mathfrak{R}_s > 0$ and $\lambda \leq \frac{27\pi^4}{49\mathfrak{R}_s} (1 + \delta)$, then $p_r < 0$.

Proof : Follows from Theorem 1.

Corollary 1 implies that oscillatory motions of growing amplitude are not allowed in magnetorotatory double-diffusive instability of Veronis type if the initial stability parameter λ doesn't exceed the value $\frac{27\pi^4}{4\mathfrak{R}_s}(1+\delta)$. Further, this result is uniformly valid for an initially top heavy as well as an initially bottom heavy configuration.

Remarks : The following remarks, now, deserve attention :

- (a) If $0 < \mathfrak{R} \leq \mathfrak{R}_s \leq \frac{27\pi^4}{4}(1+\delta)$ and $p_r \neq 0$, then Corollary 1 implies that $p_r < 0$.
- (b) If $0 < \mathfrak{R} \leq \frac{27\pi^4}{4}(1+\delta) < \mathfrak{R}_s$ and $p_r \neq 0$, even then Corollary 1 implies that $p_r < 0$.

It is easy to see that

- (i) $\delta = \frac{\tau}{\sigma}$ for VTC, (ii) $\delta = \min\left(\frac{\tau}{\sigma}, \frac{1}{\sigma_1}\right)$ for hydromagnetic VTC, and
- (iii) $\delta = \min\left(\frac{\tau}{\sigma}, 1\right)$ for rotatory VTC. Consequently, the characterization theorem of Banerjee *et al.*⁸ and Gupta *et al.*⁹ for VTC can easily be averred from (a). Further, in case of rotatory VTC and hydromagnetic VTC (a) yields more general results than those derived by Banerjee and co-authors^{4,5}

The above remarks thus clearly and unequivocally establish the generality of the results derived herein.

Theorem 2 (A semi-circle theorem for magnetorotatory STC) :

If $(p, w, \theta, \phi, h_z, \zeta, \xi) p = p_r + ip_i, p_r \geq 0, p_i \neq 0$, is a nontrivial solution of eqn. (1) - (6) together with the boundary conditions (7), and $\mathfrak{R} < 0, \mathfrak{R}_s < 0$, then

$$|p| < \frac{\hat{\lambda}|\mathfrak{R}|}{4\pi^2(1+\hat{\delta})} \sqrt{\hat{\Omega}^2 - 1}, \quad \hat{\delta} = \min\left(\frac{1}{\sigma}, \frac{1}{\sigma_1}, 1\right) \text{ and } \hat{\lambda} = \frac{|\mathfrak{R}_s|}{|\mathfrak{R}|}.$$

Proof. Replacing \mathfrak{R} and \mathfrak{R}_s by $-|\mathfrak{R}|$ and $-|\mathfrak{R}_s|$ respectively in eqn. (1) and proceeding exactly as in Theorem 1, *mutatis mutandis*, we get the desired result.

Corollary 2 : If $(p, w, \theta, \phi, h_z, \zeta, \xi) p = p_r + ip_i$, $p_i \neq 0$, is nontrivial solution of eqn. (1) – (6) together with the boundary conditions (7) and $\mathfrak{R} < 0$, $\mathfrak{R}_s < 0$ and $\hat{\lambda} \leq \frac{27\pi^4\tau}{4|\mathfrak{R}|} (1 + \hat{\delta})$, then $p_r < 0$.

Proof: Follows from Theorem 2.

The essential contents of Theorem 2 and Corollary 2 from the point of view of hydrodynamic stability are similar to those of Theorem 1 and Corollary 1. However, now they pertain to magnetorotatory double-diffusive instability of Stern type. Further remarks similar to those after Corollary 1 hold here also. To be specific, Corollary 2 implies that .

(a) If $0 < |\mathfrak{R}_s| \leq |\mathfrak{R}| \leq \frac{27\pi^4\tau}{4} (1 + \hat{\delta})$ and $p_i \neq 0$, then $p_r < 0$.

(b) If $0 < |\mathfrak{R}_s| \leq |\mathfrak{R}| \leq \frac{27\pi^4\tau}{4} (1 + \hat{\delta}) < |\mathfrak{R}|$ and $p_i \neq 0$ even then $p_r < 0$.

Further, it is easy to see that

(i) $\hat{\delta} = \frac{1}{\sigma}$ for STC, (ii) $\hat{\delta} = \min\left(\frac{1}{\sigma}, \frac{1}{\sigma_1}\right)$ for hydromagnetic STC, and

(iii) $\hat{\delta} = \min\left(\frac{1}{\sigma}, 1\right)$ for rotatory STC. Consequently, one can easily write down from Corollary 2 the characterization theorems for STC with or without the individual effects of a rotation and a magnetic field.

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Dedication

This paper is dedicated to the sweet and everlasting memories of Anoop Gupta (son of the first author).

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Convective instability in a horizontal fluid layer

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Abstract

Linear thermal stability of a horizontal fluid layer confined between two rigid boundaries and heated from below is considered. The temperature distribution between the walls consists of the two parts a steady part and a time-dependent oscillatory part. Disturbances are assumed to be infinitesimal. Only odd solutions are considered. Floquet theory is used to study the stability of the solution. Numerical results for the critical Rayleigh number are obtained. It is found that the disturbances are either synchronous with the primary temperature field or have half its frequency.

(Keywords : modulation/ stability/ rayleigh number/ odd solution/thermal convection)

Introduction

This paper deals with the stability of a horizontal fluid layer confined between two rigid planes. The layer is heated from below and the temperature of the lower and the upper plates varies periodically with time. Study of convective flow is of great importance in geophysics and industrial operations. Considerable attention has been given to this problem during the last fifty years. Chandrasekhar¹ has given a comprehensive review of this stability problem with steady temperature gradient. Venezian², who worked out the thermal analogue of Donnelly's experiment³, was the first to consider the oscillatory temperature profile for modulating the wall temperatures, nevertheless a similar problem had been considered earlier by Gershuni and Zhukhovitskii⁴ for a temperature profile, obeying rectangular law. Later on many investigators studied this problem of thermal convection under various physical

conditions, considering different temperature profiles and boundary conditions. Some of them are : Rosenblat and Herbert⁵, Rosenblat and Tanaka⁶, Yih and Li⁷, Gresho and Sani⁸, Finucane and Kelly⁹, Roppo *et al.*¹⁰ and Aniss *et al.*¹¹. Recently author's group¹²⁻¹⁶ has investigated the convective instability using sinusoidal function, saw-tooth function, step-function and day-night function for modulation of the wall temperatures.

The objective of the present analysis is to determine the critical conditions under which convective instability can occur. The effect of temperature modulation on the stability limit of the system has also been investigated. Only odd solutions have been considered. The results have their relevance with convective flows in the terrestrial atmosphere

Formulation

Consider a fluid layer of a viscous, incompressible fluid, confined between two parallel horizontal walls, one at $z = -d/2$ and the other at $z = d/2$. The walls are infinitely extended and rigid. Then using normal mode technique, the non-dimensionalized, linear governing equations, in the Boussinesq approximation are

$$\omega \left(D^2 - a^2 \right) \frac{\partial w}{\partial \tau} = -P\theta + P(D^2 - a^2)^2 w \quad (1)$$

$$\omega \frac{\partial \theta}{\partial \tau} = (D^2 - a^2)\theta - Ra^2 \left(\frac{\partial T}{\partial z} \right) w \quad (2)$$

where $D = \frac{\partial}{\partial z}$, perturbation quantities $V = (u, v, w)$, θ and p are respectively, the fluid velocity, temperature and pressure fields. T is the temperature in the conducting state while τ is the time. $P = v/k$ is the Prandtl number, $R = \alpha g \Delta T d^3 / v k$ is the Rayleigh number, α is the coefficient of volume expansion, g is the acceleration due to gravity, ΔT is the temperature difference between the walls, v is the kinematic viscosity, k is the thermal diffusivity, ω is the non-dimensional frequency, and a is the horizontal wave number.

The considered boundary conditions in the non-dimensional form are given by

$$T = 1 - \varepsilon \cos \tau \quad \text{at} \quad z = -\frac{1}{2} \quad (3a)$$

$$= \varepsilon \cos \tau \quad \text{at} \quad z = \frac{1}{2} \quad (3b)$$

where ε is the amplitude of modulation. Then the temperature gradient $\frac{\partial T}{\partial z}$ is found to be

$$\frac{\partial T}{\partial z} = -1 + \varepsilon R_e \{ F(z, \tau) \} \quad (4)$$

$$\text{where } F(z, \tau) = \frac{\lambda \cos h(\lambda z)}{\sin h(\lambda/2)} e^{\iota \tau} \quad \text{and} \quad \lambda^2 = \iota \omega \quad (5)$$

The boundary conditions on w and θ are

$$w = Dw = 0 \quad \text{at} \quad z = \pm \frac{1}{2} \quad (6)$$

$$\theta = 0 \quad \text{at} \quad z = \pm \frac{1}{2} \quad (7)$$

Method

Expression (5) shows that $F(z, t)$ is an even function of z . By carefully analyzing the eqns. (1) and (2) and the boundary conditions (6) and (7) we see that the proper solution of the eqns. (1) and (2) can be divided into two non-combining groups of even and odd solutions. Previous investigations^{17,18} on thermal convection have shown that disturbances corresponding to even solutions are most unstable; however here we discuss the stability of the disturbances corresponding to odd solutions.

Now since θ vanishes at $z = \pm \frac{1}{2}$, therefore it is expanded in a series of $\sin(2n\pi z)$

Also w is written in a series of ϕ_n so that

$$(D^2 - a^2)^2 \phi_n = \sin(2n\pi z) \quad (8)$$

$$\text{where } \phi_n = D\phi_n = 0 \quad \text{at } \pm \frac{1}{2} \quad (9)$$

Then the general solution (8) can be given by

$$\phi_n = P_n \sinh a z + Q_n \cosh a z + \gamma_n^2 \sin(2n\pi z) \quad (10)$$

$$\text{where } P_n = (-1)^n \frac{2n\pi\gamma_n^2}{\sinh a - a} \cosh(a/2) \quad (11)$$

$$Q_n = -(-1)^n \frac{4n\pi\gamma_n^2}{\sinh a - a} \sinh(a/2) \quad (12)$$

$$\text{and } \gamma_n = \frac{1}{4n^2\pi^2 + a^2} \quad (13)$$

The expansions for w and θ can be written as

$$w(z, \tau) = \sum_{n=1}^{\infty} A_n(\tau) \phi_n(z) \quad (14)$$

$$\theta(z, \tau) = \sum_{n=1}^{\infty} B_n(\tau) \sin(2n\pi z) \quad (15)$$

Now substitute (14) and (15) into the eqns. (1) and (2), and multiply by $\sin(2m\pi z)$ resulting equations are then integrated with respect to z in the interval $\left(-\frac{1}{2}, \frac{1}{2}\right)$. The

outcome is a system of ordinary differential equations for the unknown coefficients $A_n(\tau)$ and $B_n(\tau)$.

$$\omega \sum_{n=1}^{\infty} [K_{nm} - \alpha^2 P_{nm}] \frac{dA_n}{d\tau} = -\frac{P}{2} B_m + P \sum_{n=1}^{\infty} [L_{nm} - 2\alpha^2 K_{nm} + \alpha^4 P_{nm}] A_n \quad (16)$$

$$\frac{\omega}{2} \frac{dB_m}{d\tau} = -\frac{1}{2} [(2m\pi)^2 + \alpha^2] B_m + Ra^2 \sum_{n=1}^{\infty} [P_{nm} - b \operatorname{Re}\{F_{nm} e^{i\tau}\}] A_n \quad (17)$$

$$(m=1, 2, 3, \dots, \dots)$$

The other coefficients, which occur in (16) and (17) are

$$P_{nm} = \int_{-1/2}^{1/2} \phi_n(z) \sin(2m\pi z) dz \quad (18)$$

$$K_{nm} = \int_{-1/2}^{1/2} D^2 \phi_n(z) \sin(2m\pi z) dz \quad (19)$$

$$L_{nm} = \int_{-1/2}^{1/2} D^4 \phi_n(z) \sin(2m\pi z) dz \quad (20)$$

$$F_{nm} = \frac{\lambda}{\sin h(\lambda/2)} \int_{-1/2}^{1/2} \phi_n(z) \cos h(\lambda z) \sin(2m\pi z) dz \quad (21)$$

Here the values of the integrals (18)-(20) have been obtained in their closed forms, however (21) has been calculated numerically, using Simpson's (1/3)rd rule¹⁹. Thus

$$P_{nm} = \frac{1}{2} \gamma_n^2 \delta_{nm} + (-1)^m 2m\pi \gamma_m [2P_n \sinh(\alpha/2) + Q_n \{\cosh(\alpha/2) - 4\alpha \gamma_m \sinh(\alpha/2)\}] \quad (22)$$

$$K_{nm} = -\frac{1}{2} \gamma_n^2 (2m\pi)^2 \delta_{nm} + (-1)^m 2m\pi \gamma_m [2(\alpha^2 P_n + 2\alpha Q_n) \sinh(\alpha/2) + \alpha^2 Q_n \{\cosh(\alpha/2) + 4\alpha \gamma_m \sinh(\alpha/2)\}] \quad (23)$$

$$L_{nm} = \frac{1}{2} \gamma_n^2 (2n\pi)^4 \delta_{nm} + (-1)^m 2m\pi\gamma_m [2a^4 P_n \sinh(a/2) + Q_n \{4a^3 (2 - a^2 \gamma_m) \sinh(a/2) + a^4 \cosh(a/2)\}] \quad (24)$$

where δ_{nm} is the Kronecker delta.

It is convenient for computational purpose to take $m = 1, 2, 3, \dots, N$ i.e. total $2N$ equations and then rearrange them. For this, multiply the eqns. (16) by the inverse of the matrix $(K_{nm} - a^2 P_{nm})$, and then introduce the notations

$$x_1 = A_1, x_2 = B_1, x_3 = A_2, x_4 = B_2 \quad (25)$$

Now combine the eqns. (16) and (17) to the form

$$\frac{dx_i}{dt} = H_{i1}x_1 + H_{i2}x_2 + \dots + H_{iL}x_L \quad (26)$$

$$(i = 1, 2, 3, \dots, 2N \text{ and } L = 2N)$$

where $H_i(t)$ is the matrix of the coefficients in the eqns. (16) and (17).

Analysis

Since the coefficients $H_i(\tau)$ of the eqns. (26) are either constant or periodic in τ with period $\tau_0 = 2\pi/\omega$, therefore the stability of the solution of (26) can be discussed on the basis of the Floquet theory²⁰. The solution in Floquet theory must be of the form $e^{\mu\tau} P(\tau)$, where $P(\tau)$ is a periodic function of τ with period τ_0 . The vanishing of the real part μ_r of μ gives the stability boundary. Here our aim is to determine the conditions under which $\mu_r = 0$. The disturbance is synchronous with the unsteady part of the mean temperature field, if the imaginary part $\mu_i = 0$. The disturbance is synchronous with the unsteady part of the mean temperature field, if the imaginary part μ_i of μ is zero. However if $\mu_i \tau_0$ is equal to π or $-\pi$, then the disturbance is subharmonic, having frequency half that of the unsteady mean temperature field.

Let

$$x_n(\tau) = x_{in}(\tau) = \text{col}[x_{1n}(\tau), x_{2n}(\tau), \dots, -x_{Ln}(\tau)] \quad (27)$$

$$(n=1, 2, 3, \dots, 2N)$$

be the solutions of (26) which satisfy the initial conditions

$$x_{in}(0) = \delta_{in} \quad (28)$$

The solutions (27) with the conditions (28) form $2N$ linearly independent solutions of the eqn. (26). Once these solutions are found, one can get the values of $x_{in}(2\pi)$ and then arrange them in the constant matrix

$$C = [x_{in}(2\pi)]. \quad (29)$$

The eigenvalues $\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_L$ of the matrix C are also called the characteristic multipliers of the system (26) and the number μ_r , defined by the relations

$$\lambda_r = \exp(2\pi\mu_r), \quad r = 1, 2, 3, \dots, 2N \quad (30)$$

are the characteristic exponents.

The values of the characteristic exponents determine the stability of the system. We assume that the μ_r are ordered so that

$$\text{Re}(\mu_1) \geq \text{Re}(\mu_2) \geq \dots \geq \text{Re}(\mu_L) \quad (31)$$

Then the system is stable if $\text{Re}(\mu_i) < 0$, while $\text{Re}(\mu_i) = 0$ corresponds to one periodic solution and represents a stability boundary. This periodic disturbance is the only disturbance, which will manifest itself at marginally stability.

To obtain the matrix C we have integrated the system (26) using Runge-Kutta-Gill procedure¹⁹. The eigenvalues $\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_L$ of the matrix C are found with the help of Rutishauser method²¹.

Results and Discussion

By setting n, m equal to 1 and $\epsilon = 0$ (in the absence of modulation) in eqns. (16) and (17), we find the first approximation to Rayleigh number for the onset of convection. This minimum value of Rayleigh number at a particular wave number a is the value R_{neut} , at neutral stability. This corresponds to $\sin(2\pi z)$, a trial function for θ . The corresponding value for R is

$$R = \frac{(4\pi^2 + a^2)^3}{a^2 \left[1 - 64a\pi^2 \sinh^2(a/2) / \left\{ (4\pi^2 + a^2)^2 (\sinh a - a) \right\} \right]} \quad (32)$$

which gives

$$R_{neut} = 17803.24 \text{ at } a = 5.365. \quad (33)$$

This is in contrast to the exact value 17610.39, at the same value of the wave number. The second approximation to the Rayleigh number is found to be 17621.74 at $a = 5.364$, which is obtained by setting $m, n = 1$ and 2. Similarly the third approximation, obtained by putting $n, m=1, 2, 3$ is 17611.84 at $a = 5.364$. These values are same, as they should, to the Chandrasekhar's values¹. By including more terms in the expansion of w and θ one can achieve a higher degree of accuracy. With the help of the available packages one could carry out these calculations more accurately.

The solution is obtained by solving the system (26) for x_1, x_2, x_3 and x_4 . Now we calculate the modified value of R_c : (the critical Rayleigh number) with variation in other parameters and check the critical value of the wavenumber a , for the case when $\epsilon \neq 0$. Here the results are calculated for moderate values of ϵ as we are interested only in the modulating effect of the oscillation, there seems to be no reason why this theory can not be applied for large values of the parameters.

We obtain a relationship between the critical Rayleigh number R_c and the corresponding critical wavenumber a_c in terms of the other parameters P, ϵ and the dimensionless frequency ω . The critical Rayleigh number is the minimum value of R as a function of the wavenumber a with variation in parameters P, ϵ and ω . The corresponding value of a is known as the critical wavenumber a_c . To obtain the critical curve R_c versus ϵ (Fig. 1) we proceed as follows: First fix P and ω , then for some value of ϵ , find that value of the wavenumber for which R is minimum. This

minimum value of R and the corresponding value of the wavenumber are the critical Rayleigh number and the critical wavenumber respectively. Continue in this way we find R_c and the corresponding a_c for different values of ε . Thus we get a curve R_c versus ε , for fixed values of P and ω . The curve consists of two different curves, one corresponding to synchronous solution (S-curves) having same frequency as the applied temperature field and the other corresponding to subharmonic solution (H-curve) having frequency half that of the applied temperature field.

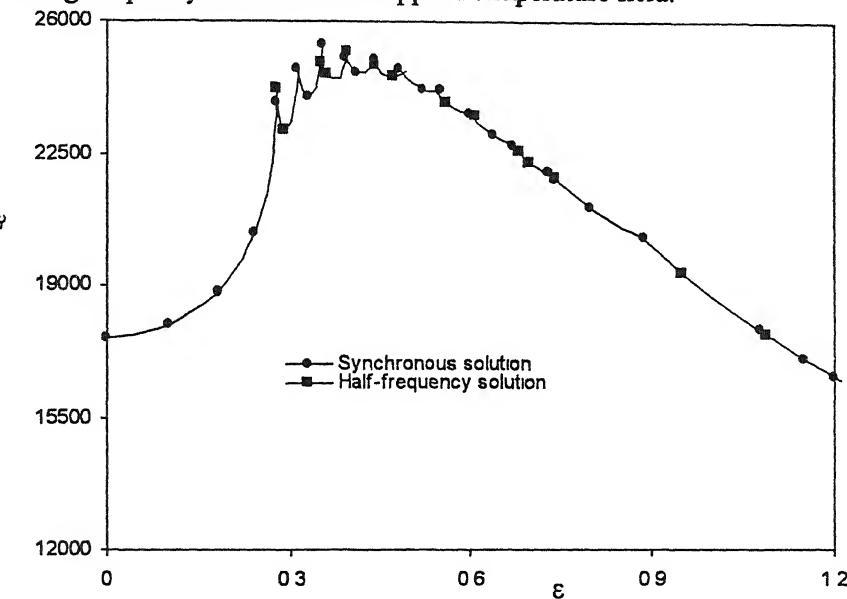


Fig. 1—Variation of R_c with ε $\omega=5.0$, $P=0.73$.

Also we calculate the modified value of R_{neut} (R at $a=5.364$) with variation in other parameters and check the critical value of the wavenumber at neutral stability. Since R_c is the minimum value of R at some wavenumber (a_c) while R_{neut} is the value of R at $a=5.364$, therefore R_c is always less than R_{neut} , but they coincide when $\varepsilon=0$ (in the absence of modulation).

In Fig. 1 we have shown the variation of the critical Rayleigh number R_c , with ε at $\omega=5.0$ and $P=0.73$. The graph consists S -curves and H -curves alternatively, which are intersecting at the cusps. Thus in the area above H -curve there are also synchronous disturbances, but disturbances with half-frequency can be expected to be more unstable. Similarly above an S -curve there are disturbances with half frequency but synchronous disturbances are more unstable.

It is clear from the Fig 1 that initially in the synchronous region where ϵ small, convection occurs at higher Rayleigh number than in the unmodulated case($\epsilon=0$, $R_c=17621.74$), so the effect of modulation on the stability of the system is stabilizing. Also the critical Rayleigh number increases as ϵ increases so the modulating effect becomes more and more stabilizing. But on further increasing ϵ we get alternatively H -curve and S -curve and the critical Rayleigh number R_c decreases. The value of R_c decreases with increasing ϵ and a stage is reached beyond which($\epsilon=1.1$) the value of R_c becomes less than 17621.74(unmodulated case), therefore convection occurs at lower Rayleigh number than in unmodulated case and the effect of modulation becomes destabilizing. With further increasing ϵ , the modulation effect becomes more and more destabilizing as R_c decreases continuously.

The results are in agreement with the findings of Yih and Le⁷. It also agrees with the results of Rosenblat and Tanaka⁶ and Bhaduria and Bhatia¹⁴ who found that the effect of the out of phase modulation of the temperature field is stabilizing. Comparing the results of Rosenblat and Bhatia⁶ and Bhaduria and Bhatia¹⁴ with the above results we see that their curves are smooth while here we have alternative S -curve and H -curve. Initially upto $\epsilon=0.28$ we have a smooth curve and then alternative H -curve and S -curve. As we go beyond a certain value of ϵ we find a destabilizing effect, however in their cases the stabilization effect increases with ϵ . This difference may be because here the boundary conditions are slightly different from theirs. The above results also agree with the findings of Venezian² and Bhatia and Bhaduria¹⁵ who found that for out of phase modulation, initially the effect of unsteady part is stabilizing but becomes destabilizing at a particular P as ω increases. The results are in agreement with that of Yih and Li⁷ who found while studying the instability of unsteady flow that initially the effect of modulation is stabilizing and later on it becomes destabilized. They also found that the critical curve is composed of the two curves, one corresponding to synchronous solution and the other corresponds to subharmonic one. We also check the variation of the critical wavenumber a_c with respect to ϵ , corresponding to the critical Rayleigh number R_c in Fig. 1. The critical value a_c appears to be discontinuous, as in Fig. 1, S -curves and H -curves are not continued beyond their intersections. The existence of synchronous and subharmonic disturbances has already been indicated by Gresho and Sani⁸, Yih and Li⁷, Clever *et al.*²² and Aniss *et al.*¹¹ in their investigations.

Fig. 2 depicts the value of the Rayleigh number R_{neut} (at neutral stability) with respect to ϵ at $a=5.36$. Therefore the value of R_{neut} is slightly greater than the value of R_c in Fig 1. However the values of R in both the figures do not differ much, as the values of a_c corresponding to Fig. 1 are never very much different from 5.36. In Fig. 3

we consider the variation of R_{neut} with ω at $P = 0.73$ and $\varepsilon = 0.1$. The effect of modulation is found to be stabilizing, decreasing with increasing frequency ω . As ω approaches infinity the effect of the unsteady part of the primary temperature field disappears altogether. These results are in agreement with that of Bhatia and Bhaduria¹⁵, Bhaduria and Bhatia¹⁴, Rosenblat and Tanaka⁶ and Venezian².

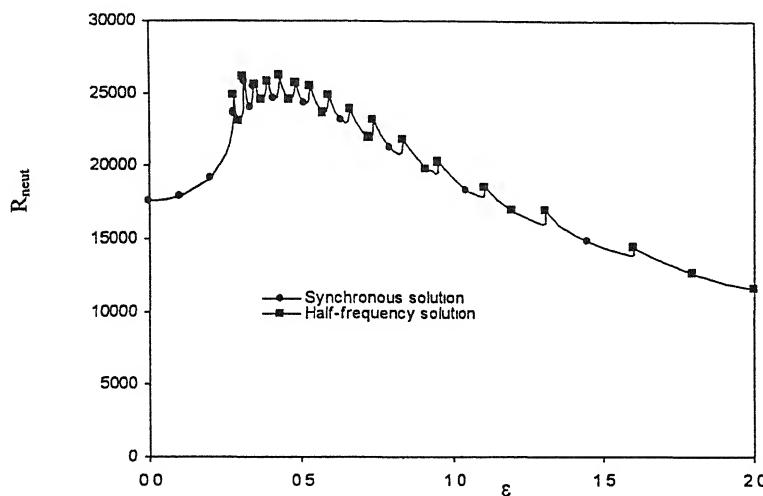


Fig. 2- Variation of R_{neut} with ε $\omega=5.0$, $P=0.73$, $a = 5.363808$

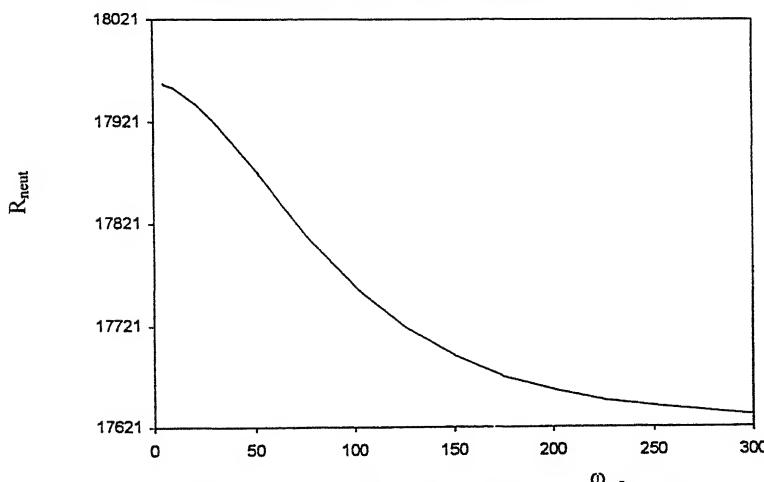


Fig. 3- Variation of R_{neut} with ε $\omega=0.1$, $P=0.73$, $a = \frac{\omega}{5.363808}$

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Hydromagnetic free convection of a particulate suspension from a permeable inclined plate with heat absorption

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Abstract

The problem of steady, laminar, free convection flow of a particulate suspension over an infinite, permeable, inclined and isothermal flat plate in the presence of a transverse magnetic field and fluid heat absorption effects is studied. An analytical solution is developed in the absence of particle loading and with constant particle phase density. A parametric study depicting the influence of the magnetic field and heat absorption effects is presented. The results for velocity, temperature and skin-friction co-efficients for both phases as well as the Nusselt number are illustrated graphically.

(Keywords hydromagnetic free convection/ particulate suspension/permeability)

Introduction

The study of free convection in porous media of an electrically conducting fluid past porous plate under the influence of a magnetic field has attracted many authors in view of its applications to geophysics, astrophysics and controlled nuclear fusion and geothermal energy for power production. Moreau¹ and other researchers have reported a large bulk of solutions and results for such flows. The study of dynamics of fluids with suspensions helps in understanding the scientific and engineering problems involved in pollution of city air, transport of suspended solid materials in pipes, motion of aerosols in the upper atmosphere of the rotating earth etc. Cheng and his associates² have extensively studied free convection and mixed convection about surfaces embedded in porous medium. In these analysis boundary layer approximations are used and Power law variations of wall temperature distribution are assumed. Thangaraj³ studied on mixed convection about inclined surfaces in porous media with variable heat flux and Dandapat and Gupta⁴ worked on longwaves on a

layer of a visco-elastic fluid down an inclined plane Acharya *et al.*⁵ have studied effects of chemical and thermal diffusion with Hall current on unsteady hydromagnetic flow near an infinite vertical porous plate. Dash and Rath⁶ have studied applying explicit finite difference scheme for flow and heat transfer of an electrically conducting fluid Acharya *et al.*⁷ further studied a problem relating to heat and mass transfer over an accelerating surfaces. Recently Acharya *et al.*⁸ studied magnetic field effect on the free convection and mass transfer flow through porous medium. Mishra⁹ have solved two-dimensional stagnation point flow of a dusty fluid near an oscillating plate. However, a few works are reported, so far as we are aware, about the hydro magnetic free convection of a particulate suspension from a permeable inclined plate for non-uniform particle-phase density.

The object of this paper is to study the steady, laminar, free convection flow of a particulate suspension over an infinite, inclined and isothermal flat plate in the presence of a transverse magnetic field and fluid heat absorption

Mathematical Analysis and Formulation of the Problem

We consider the steady, laminar, hydro magnetic free convection flow of a fluid particulate suspension over an isothermal and permeable infinitely long inclined flat plate. Uniform fluid phase suction is imposed at the plate surface. Further an uniform magnetic field is applied normal to the flow direction. The fluid phase is assumed to be stagnant and is maintained at a constant temperature T_∞ , while particle phase is having an uniform density distribution and is affected by the gravitational force far away from the plate.

The fluid is assumed to be Newtonian, electrically conducting and heat absorbing and retains constant properties except for the density in the buoyancy term. The induced magnetic and electric fields as well as the Hall effect of magnetohydrodynamics are all assumed to be negligible and the magnetic Reynold's number, electrical displacement and convection are all assumed to be small. Only the fluid phase will be affected by the presence of magnetic field since it is assumed to be electrically conducting. However, the particle phase will not be affected by that field directly since it is assumed to be electrically non-conducting (insulator). But it will be influenced indirectly by the magnetic field due to the interphase drag mechanism between the phases.

In the present study the particle phase is assumed to be made of non-uniformly distributed spherical particles all having one size and with a constant viscosity and diffusivity properties. The particle phase viscosity can be considered as a natural

consequence of the averaging process involved in representing a discrete system of particles as a continuum^{10,11}. Also, the particle-phase viscous effects can be used to make particle-particle interaction and particle-wall interaction in relatively dense suspensions. These effects have been investigated previously by many authors such as Tsuo and Gidaspow¹² and Gadiraju *et al.*¹³. Both the fluid and particle phases are taken as interacting continuously exchanging both momentum and heat transfer as discussed by Marble¹⁴. The volume fraction of suspended particles is considered small compared to that of the fluid phase.

The governing equations for the present problem are based on the conservation of mass, linear momentum, and energy for both the fluid and the particle phases. With above frame of references and assumptions (the plate is infinite in extent and the flow is steady), the physical variables are functions of y only. Thus, the governing equations are given by

$$\frac{dv}{dy} = 0 \quad (1)$$

$$\mu \frac{d^2u}{dy^2} - \rho v \frac{du}{dy} - \frac{dP}{dx} - \rho_p N(u - u_p) - \rho g \cos \phi - \sigma_0 B_0^2 u = 0 \quad (2)$$

$$k \frac{d^2T}{dy^2} - \rho cv \frac{dT}{dy} + \rho_p c_p N_T (T_p - T) + q_0 (T - T_\infty) = 0 \quad (3)$$

$$D_p \frac{d^2 \rho_p}{dy^2} - \frac{d(\rho_p v_p)}{dy} = 0 \quad (4)$$

$$\nu_p \frac{d}{dy} \left(\rho_p \frac{du_p}{dy} \right) - \rho_p v_p \frac{du_p}{dy} + \rho_p N(u - u_p) - \rho_p g \cos \phi = 0 \quad (5)$$

$$2\nu_p \frac{d}{dy} \left(\rho_p \frac{dv_p}{dy} \right) - \rho_p v_p \frac{dv_p}{dy} + \rho_p N(v - v_p) - \rho_p g \sin \phi = 0 \quad (6)$$

$$\frac{k_p}{\rho_p} \frac{d}{dy} \left(\rho_p \frac{dT_p}{dy} \right) - \rho_p c_p v_p \frac{dT_p}{dy} - \rho_p c_p N_T (T_p - T) = 0 \quad (7)$$

where

B_0 Magnetic induction, C : Fluid-phase specific heat, C_f : Fluid-phase skin friction co-efficient, D : Diffusion co-efficient, f : Any dependent variable, g . Acceleration due to gravity, Gr : Grashof number, H : Dimensionless gravitational acceleration, k Fluid-phase thermal conductivity, L : Characteristic length, M : Hartmann number, N : Interphase momentum transfer co-efficient, N_T : Interphase heat transfer co-efficient, N_u Nusselt Number, P : Fluid-phase pressure, Pr : Fluid-phase Prandtl number, q_0 . Dimensional heat absorption co-efficient, Q_p : Dimensionless particle-phase density, R_v : Wall suction velocity, S : Dimensionless heat absorption coefficient, S_c : Inverse Schmidt number, T . Fluid-phase temperature, u . Fluid-phase x -component of velocity, U Fluid-phase dimensionless tangential velocity, v : Fluid-phase y -component of velocity, V . Fluid-phase dimensionless normal velocity, x, y . Cartesian co-ordinates, Y : Dimensionless normal distance,

Greek Symbols

- α Velocity inverse Stokes number
- β Particle-phase to fluid Viscosity ratio
- β Volume expansion co-efficient
- γ Specific heats ratio
- ε Temperature inverse Stokes number
- θ Fluid-phase dimensionless temperature
- K Particle loading
- μ Fluid-phase dynamic viscosity
- ν Fluid-phase Kinematic viscosity
- ρ Fluid-phase density
- σ_0 Fluid-phase electrical conductivity
- ϕ Tilt angle
- ω Particle-phase wall slip co-efficient
- Ω_p Particle phase

(ω) Plate wall

(∞) Very large distance away from the plate surface (ambient condition)

The boundary conditions are

$$v(0) = -v_w$$

$$u(0) = 0 \quad u(\infty) = 0$$

$$T(0) = T_w \quad T(\infty) = T_\infty$$

$$\rho_P(0) = \rho_{Pw} \quad \rho_P(\infty) = \rho_{P\infty}$$

$$u_P(0) = \omega_s \frac{du_P}{dy} \Big|_{y=0} \quad u_P(\infty) = \frac{-g}{N} \cos \phi$$

$$T_P(0) = T_w \quad T_p(\infty) = T_\infty \quad (8)$$

where ω_s is the dimensional particle-phase wall slip co-efficient. Since the particle-phase may resemble a rarefied gas and undergoes slip at a boundary. Following Soo¹⁷ and Chamkha¹⁸ we have specified the boundary conditions in the present problem

The hydrostatic pressure gradient in eqn. (2) is approximated as

$$\frac{dP}{dx} = \rho_{P\infty} Nu_{P\infty} - \rho_\infty g \cos \phi \quad (9)$$

where

$$u_{P\infty} = \frac{-g \cos \phi}{N} \quad (10)$$

This approximation can be easily obtained by evaluating eqns. (1)-(7) as $y \rightarrow \infty$. Using Boussineq approximation to couple the fluid momentum eqn. to the temperature field and substituting eqns. (9) and (10), eqn. (2) can be written as

$$\begin{aligned}
& \frac{\mu d^2 u}{dy^2} - \rho_\infty v \frac{du}{dy} - \rho_p N(u - up) + \rho_{p\infty} g \cos \phi \\
& + \rho_\infty g \bar{\beta} (T - T_\infty) \cos \phi - \sigma_0 B_0^2 u = 0
\end{aligned} \tag{11}$$

Introducing the dimensionless quantities

$$\begin{aligned}
Y &= \frac{y Gr^{\frac{1}{4}}}{L}, & U &= \frac{uL}{v Gr^{\frac{1}{2}}}, & V &= \frac{vL}{v Gr^{\frac{1}{4}}}, \\
U_p &= \frac{u_p L}{v Gr^{\frac{1}{2}}}, & V_p &= v_p \frac{L}{v Gr^{\frac{1}{4}}}, & \theta &= \frac{T - T_\infty}{T_w - T_\infty}, \\
Q_p &= \frac{T_p - T_\infty}{T_w - T_\infty}, & Q_p &= \frac{\rho_p}{\rho_{p\infty}}, & S &= \frac{q_0 L^2}{\mu c Gr^{\frac{1}{2}}}, \\
K &= \frac{\rho_{p\infty}}{\rho_\infty}, & \alpha &= \frac{NL^2}{v Gr^{\frac{1}{2}}}, & H &= \frac{gL^3}{v^2 Gr}, \\
\gamma &= \frac{C_p}{c}, & \epsilon &= \frac{N_t L^2}{v Gr^{\frac{1}{2}}}, & \beta &= v_p/v \\
M^2 &= \frac{\sigma_0 B_0^2 L^2}{\mu Gr^{\frac{1}{2}}}, & Pr &= \mu \frac{c}{k}, & Pr_p &= \frac{\mu_p c_p}{k_p}, \\
Sc &= \frac{D_p}{v}, & Gr &= \frac{g \bar{\beta} (T_w - T_\infty) L^3}{v^2} & & \tag{12}
\end{aligned}$$

the eqns. (1,4) and (6) reduce to

$$\frac{dV}{dY} = 0 \quad (13)$$

$$Sc \frac{d^2 Q_P}{dY^2} - V_P \frac{dQ_P}{dY} = 0 \quad (14)$$

$$2\beta \frac{d}{dY} \left(Q_P \frac{dV_P}{dY} \right) - Q_P V_P \frac{dV_P}{dY} + \alpha Q_P (V - V_P) + HGr^{1/4} Q_P \sin \phi = 0 \quad (15)$$

Now the dimensionless boundary conditions are

$$V(0) = -Rv,$$

$$U(0) = 0, \quad U(\infty) = 0$$

$$\theta(0) = 1, \quad \theta(\infty) = 0$$

$$Q_P(0) = Q_{P0}, \quad Q_P(\infty) = 1$$

$$U_P(0) = \omega \frac{dU_P}{dY} \Big|_{Y=0}, \quad U_P(\infty) = -\frac{H}{\alpha} \cos \phi$$

$$\theta_P(0) = 1, \quad \theta_P(\infty) = 0, \quad (16)$$

where $R_v = v_w L / \nu Gr^{1/4}$ and $\omega = \omega_s Gr^{1/4} / L$ are the dimensionless fluid phase suction velocity and the particle-phase slip co-efficient. Here all R_v, Q_{P0} and ω are assumed to be constant.

The fluid-phase skin friction co-efficient C_f , the particle-phase skin friction co-efficient C_{fP} and the Nusselt number Nu are defined, respectively as

$$C_f = \frac{\mu \frac{du}{dy} \Big|_{y=0}}{\frac{1}{2} \rho \left(\frac{v}{L} \right)^2 Gr^{3/4}} = 2 \frac{dU}{dY} \Big|_{Y=0} \quad (17)$$

$$C_{fP} = \frac{\mu_P \frac{du_P}{dy} \Big|_{y=0}}{\frac{1}{2} \rho \left(\frac{v}{L} \right)^2 Gr^{3/4}} = 2K\beta \frac{dU_P}{dY} \Big|_{Y=0} \quad (18)$$

$$Nu = \frac{hL}{kGr^{1/4}} = - \frac{d\theta}{dY} \Big|_{Y=0} \quad (19)$$

Analytical Solution for Particle-Phase Density

From eqn (13) with eqn. (16) we have

$$V = -Rv \quad (20)$$

Assuming V_P is constant throughout the domain of interest and substituting eqn. (20) into eqn. (15) and rearranging we get

$$V_P = \frac{H}{\alpha} Gr^{\frac{1}{4}} \sin \phi - Rv = \pi \quad (21)$$

Obviously, for a vertical plate ($\phi=0$) both V and V_P will have the same wall suction velocity Rv .

Substituting eqn. (21) into (14) we have

$$Sc \frac{d^2 Q_P}{dY^2} - \pi \frac{dQ_P}{dY} = 0 \quad (22)$$

The solution of eqn. (22) subject to the required boundary conditions can be shown to be

$$Q_P = 1 + (Q_{P0} - 1) e^{\frac{\pi}{Sc} Y} \quad (23)$$

The solution (23) needs further elaboration, which is very important. A physically acceptable solution for Q_P requires that π be always negative. Eqn (23) being exponential, if π is allowed to attain a positive value, it will grow towards infinity without limits; which is, obviously, not a valid solution. Physically, the requirement that π be negative means that the particle-phase normal velocity must be negative i.e. towards the plate, to ensure a continuous flow of particles to compensate for the lost particles through the suction and to sustain the requirement of constant particle-phase density at the wall surface. If V_P is allowed to be positive i.e. away from the plate surface, all the particles will be cleaned away from the vicinity of the plate and the wall boundary conditions for Q_P can not be met. The requirement of π to be always negative or at most zero was also required in the analytical and numerical solutions (see Ramadan and Chamkha^{15,16}). However in order to obtain a closed form solution we have studied the present problem in the absence of particle loading (i.e. $K=0$) and with constant particle phase density (i.e. $Q_P = 1$). In our future work a numerical solution is sought for to solve the coupled non-linear equations arising out of due to particle phase loading ($K \neq 0$) and with variable particle-phase density.

With above assumption and substituting eqns. (20), (21), (12) in eqns. (2), (3), (5) and (7) and on simplification we get

$$\frac{d^2 U}{dY^2} + Rv \frac{dU}{dY} - M^2 U + \theta \cos \phi = 0 \quad (24)$$

$$Pr^{-1} \frac{d^2 \theta}{dY^2} + Rv \frac{d\theta}{dY} + S\theta = 0 \quad (25)$$

$$\beta \frac{d^2 U_P}{dY^2} - \pi \frac{dU_P}{dY} + \alpha(U - U_P) - H \cos \phi = 0 \quad (26)$$

$$\beta Pr_P \frac{d^2 \theta_P}{dY^2} - \pi \frac{d\theta_P}{dY} + \epsilon(\theta - \theta_P) = 0 \quad (27)$$

Solution

$$\theta = e^{-m_2 Y} \quad (28)$$

$$U = \frac{-\cos \phi}{m_2^2 - Rv m_2 - M^2} \left[e^{-m_2 Y} - e^{m_4 Y} \right] \quad (29)$$

$$U_P = C_2 e^{m_6 Y} - \frac{H}{\alpha} \cos \phi + \frac{A_1 e^{-m_2 Y}}{m_2^2 + \frac{\pi}{\beta} m_2 - \frac{\alpha}{\beta}} - A_1 \frac{e^{m_4 Y}}{m_4^2 - \frac{\pi}{2\beta} m_4 - \frac{\alpha}{\beta}} \quad (30)$$

$$\theta_P = e^{m_8 Y} + \frac{\varepsilon}{m_2^2 + m_2 \frac{\pi}{\beta} Pr_P - \frac{\varepsilon}{\beta} Pr_P} \quad (31)$$

where the constants, C_2 , $m_2 > 0$, $m_4 < 0$, $m_6 < 0$, $m_8 < 0$ are given in the Appendix.

Results and Discussion

Following numerical values were assigned for various physical parameters during computations.

$$Gr=10,000, Pr=0.7, Pr_P=2, Rv=0.5, H=1, \alpha=1, \beta=0.5, \varepsilon=1, \phi=15^\circ, \gamma=1, \omega=2$$

From the Fig. 1, it is observed that as the square of the Hartmann number increases both fluid phase (solid lines) and particle phase velocity (broken lines) decrease. But it is interesting to note that particle phase velocity profiles assume negative values for higher values of Hartmann number. It is further observed that in the absence of magnetic field the particle phase velocity becomes negative near the plate wall as well as far away from the wall. Consequently particle phase velocity leads to flow reversal effect due to increase in magnetic field strength. Therefore it may be concluded that increasing the Hartmann number leads to damping of the fluid and the particle phase velocity profiles. This is due to the application of a transverse magnetic field normal to the flow direction which imposes a resistive force (Lorentz force) similar to the drag force which tends to resist the fluid flow and thus reducing the velocity.

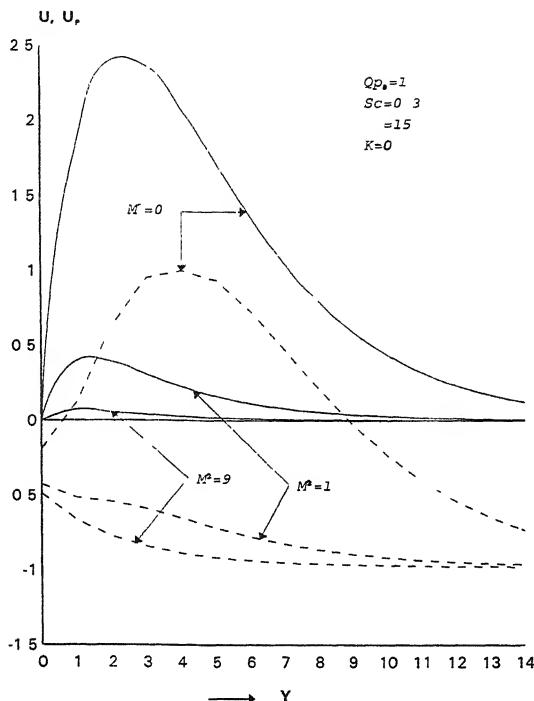


Fig. 1—Effect of Hartmann number ($S=0$); U : Fluid velocity profiles (Solid lines);
 U_p Particle phase velocity profiles (Broken lines)

It is also recorded from the numerical values of the temperature profiles that for different values of Hartmann number temperature profiles for both fluid and particle phases coincide, hence graphs are not presented here. Hence it is concluded that Hartmann number has no effect on the temperature profiles of the fluid and particle phases. Thus the Hartmann number has no effect on the Nusselt number.

The effect of heat absorption co-efficient S , are depicted in Fig. (2 & 3). It is observed that the velocity and temperature profiles for both fluid (solid lines) and particle phase (broken lines) decrease when S assumes the values 0, -1 and -3. Hence it is concluded that the effect of heat absorption is to damp the flow and heat transfer phenomena of both phases and to reduce the thickness of both the velocity and the thermal layers. This result is realistic one since, due to heat absorption, less energy is used to support the buoyancy effects while the considerable amount of energy is absorbed by the fluid. The above phenomena are clearly established as U , U_p and θ decrease as $|S|$ increases.

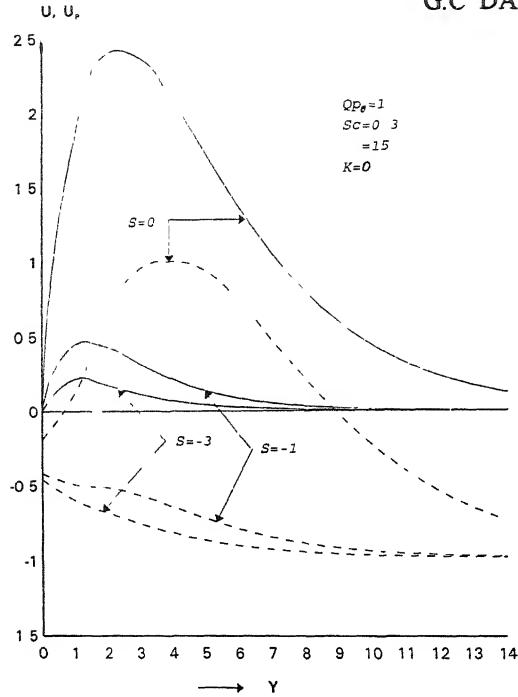
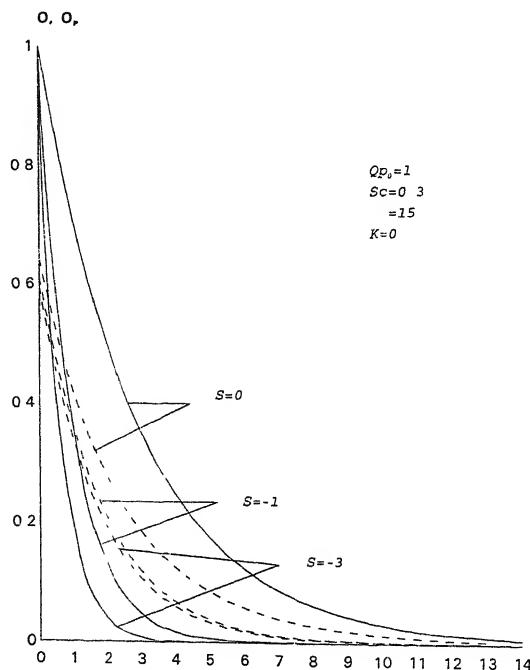


Fig. 2—Effect of heat absorption ($M=0$), U . Fluid velocity profiles (Solid lines), U_p . Particle phase velocity profiles (Broken lines)



The present study could not be undertaken in the presence of heat generation coefficient ($S > 0$) as the solution of eqn (26) does not exist

The effects of magnetic field (solid line) and the heat absorption (broken line) on the skin-friction of fluid and particle phases, C_f and C_{fp} , are shown in Fig. 4. From the eqn (18) it is seen that C_{fp} is identically zero in the absence of particle loading, ($K=0$) The decrease of C_f with the increase of magnetic field and heat absorption is noticed. This is due to the damping effect produced by magnetic field and heat absorption parameter on the flow.

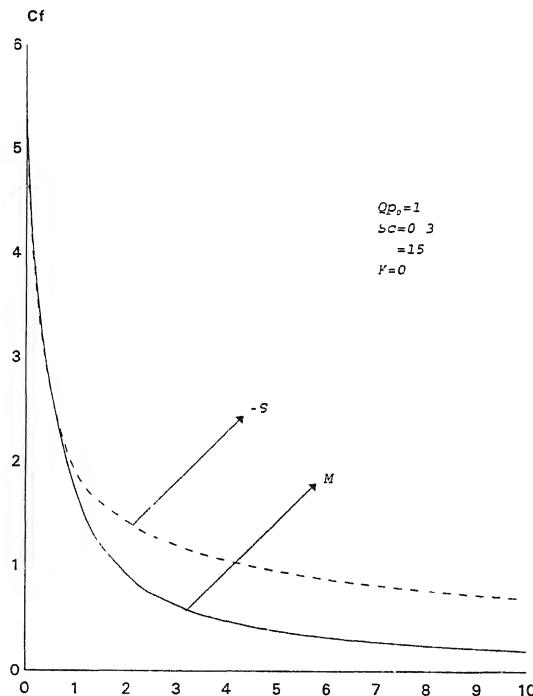


Fig. 4—Fluid-skin friction coefficient; effect of Hartmann number ($S=0$) (Solid line), effect of heat absorption ($M=0$) (Broken line)

Lastly, the effect of heat absorption on the Nusselt number is shown in Fig. 5. The Nusselt number increases with the increase of heat absorption parameter. This may be attributed to the fact that as the heat absorption increases the plate tends to supply

more energy through its wall to maintain the constant temperature of the wall, and hence the Nusselt number.

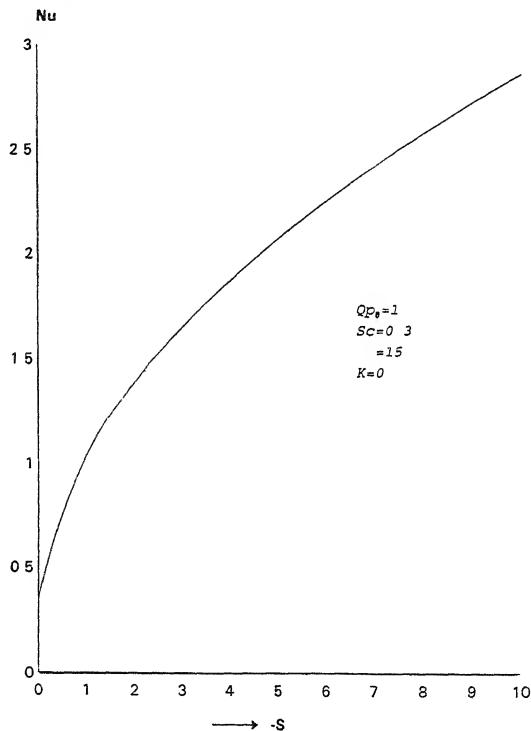


Fig. 5—Nusselt number (Effect of heat absorption ($M=0$))

Conclusion

The mathematical modelling for free convection flow of a particulate suspension over an infinite, inclined, permeable and isothermal plate in the presence of both magnetic field and fluid heat absorption was undertaken. The present study accounted for both particle viscous and diffusive effects. The general effects of the magnetic field and the heat absorbing fluid were found to damp the flow and the thermal profiles. Moreover, the Nusselt number was found to increase with the heat absorption effects but the Hartmann number has a little effect on the Nusselt number.

Appendix

$$m_2 = PrRv + \sqrt{Pr^2Rv - 4PrS}$$

$$m_4 = \frac{-Rv + \sqrt{Rv^2 + 4M^2}}{2}, \quad m_4 < 0$$

$$m_6 = \frac{1}{2} \left[\frac{\pi}{\beta} - \sqrt{\frac{\pi^2 + 4\alpha\beta}{\beta^2}} \right], \quad m_6 < 0$$

$$m_8 = \frac{1}{2} \left[\frac{\pi}{\beta} Pr_P - \sqrt{\frac{\pi^2}{\beta^2} Pr_P^2 + \frac{4\epsilon Pr_P}{\beta}} \right]$$

$$C_2 = \frac{1}{(\omega m_6 - 1)} \left[-\frac{H}{\alpha} \cos \phi + \frac{A_1(1 + \omega m_2)}{m_2^2 + \frac{\pi}{\beta} m_2 - \frac{\alpha}{\beta}} - \frac{A_1(1 - \frac{\omega}{2} m_2)}{\frac{1}{4} m_4^2 - \frac{\pi}{2\beta} m_4 - \frac{\alpha}{\beta}} \right]$$

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Orders, valuations and quadratic forms*

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Abstract

In this brief write up, we indicate without proofs the interesting results connecting the troika of the topics in the title after giving their definitions and some examples. This article is by no means exhaustive and it reflects the interests of the author.

Order

The field of rational numbers has the binary relation of order besides the two algebraic operations (addition and multiplication). This ordering is compatible with these algebraic operations. The significance of order came to the fore only in the 19th century with Cauchy and Dedekind independently developing the completion of the rational number field to real numbers, which lent rigour in real analysis, in different ways using order. Hilbert contributed to the resurgence of interest on order when he developed an axiomatic approach to geometry. However, an impetus given by Artin made the study of ordered fields a topic of great interest and utility.

We begin with the notion of an ordering P of a field K . This ordering P is subset of K having the following properties. $P + P \subseteq P$, $P \cdot P \subseteq P$, $P \cap \{-P\} = \{0\}$ and $P \cup \{-P\} = K$. It is clear that P contains (finite) sums of squares of elements of K . Generalizing this notion we define a preordering P in a commutative ring R with identity, as a proper subset P of R such that $R^2 \subseteq P$, and $P + P \subseteq P$, $P \cdot P \subseteq P$. The requirement of P as a proper subset of R may be strengthened to $-1 \notin P$.

From now on we shall restrict ourselves to the case when R is a field K . From our definition of a (pre) ordering P in K , we can immediately infer that the characteristic of K is zero (for otherwise, the characteristic is $p \neq 0$ and $-1 = 1 + 1 + \dots + 1$, $(p-1)$ times which shows $-1 \in P$, a contradiction). We also find that -1 is not a sum of squares. Given this P which is called a positive cone in case P is an ordering, we

*Dedicated to Professor R.P. Bambah

introduce an order \leq by setting $a \leq b$ in case $b - a \in P$. It is easy to verify that with the above stipulation of order, K is an ordered field. This is in the sense that the field K has a linear order (so that any two distinct elements are comparable) which is compatible with the addition and multiplication by positive elements of K .

Some examples of ordered fields.

1. The field of rational numbers \mathbb{Q} and its completion with respect to the topology induced by the metric arising out of ordinary absolute value (also known as the Euclidean topology), namely, the field of real numbers \mathbb{R} , have only one order.
2. The field $\mathbb{Q}(t)$ of rational functions over \mathbb{Q} in one variable t has uncountably many orders. This is obtained by imbedding $\mathbb{Q}(t)$ in the real field \mathbb{R} with t being mapped onto some transcendental element in \mathbb{R} over \mathbb{Q} .
3. Given the field of rational numbers \mathbb{Q} or the field of real numbers \mathbb{R} , any transcendental extension $\mathbb{Q}(t)$ ($\mathbb{R}(t)$) can be ordered by choosing as the set of positive elements those which are of the form $a \cdot t^r f(t) \cdot \{g(t)\}^{-1}$ where a is a positive element in $\mathbb{Q}(\mathbb{R})$, $f(t)$ and $g(t)$ are polynomials with constant term 1. (See Jacobson [1], pp. 272.)

Given a preorder T on a field K (or even in a ring R) we can extend it to a larger preorder, T' containing T . For this, suppose a is a non zero element of K with $-a$ not in T . Then $T' = T[a]$ which is the sub ring of K generated by T and a satisfies the conditions of a preorder. In fact a necessary and sufficient condition for this T' to be a preorder is that $a \notin -T$. Now the set of all pre-orderings P under set inclusion forms an inductive set. Using Zorn's lemma we find that any maximal element in P is indeed an ordering of K (or R).

Artin defined a field to be formally real if -1 is not expressible as a sum of squares in K . We have the following :

Theorem 1 : Let K be a field. Then K is formally real if and only if K has an ordering.

For the proof, observe that if K is formally real, then taking T as the sum of squares of elements of K , we get T as a preorder in K and this can be extended to an order as explained in the previous paragraph. For the converse, note that if K has an ordering then -1 is not a sum of squares.

Artin was led to the study of formally real fields while solving the seventeenth problem of Hilbert's celebrated problems. Hilbert² and Landau³ had shown that if α is

an algebraic integer which is positive in every real embedding of $Q(\alpha)$ in R then α is expressible as a sum of squares in $Q(\alpha)$. In fact if Γ is a finite extension of the field of rational numbers and $\{\sigma_i \mid i = 1, 2, \dots, r\}$ are the different embeddings of Γ in the field of all real algebraic numbers, then any non zero element $\gamma \in \Gamma$ is expressible as a sum of squares in Γ if and only if $\sigma_i(\gamma) < 0$ for all i .

Hilbert had shown earlier that if a rational function $\varphi(x) \in Q(x)$ $\{\varphi(x,y) \in Q(x,y)\}$ assumes nonnegative values whenever the denominator of $\varphi(x)$ (or $\varphi(x,y)\}$ does not vanish, then $\varphi(x) \{\varphi(x,y)\}$ can be expressed as a sum of 2(4) squares $\sum_{i=1}^r f_i(x)^2 \left(\sum_{j=1}^r f_j(x, y) \right)$. The 17th problem is the following :

If $\varphi(x_1, x_2, \dots, x_n)$ in $K = Q(x_1, x_2, \dots, x_n)$ is positive semi definite whenever it is defined over Q , is φ a sum of squares in K ? The quantitative aspect of this was conjectured by J. Ax in 1968 and proved by A. Pfister⁴ (positive semi definite means $\varphi(a_1, a_2, \dots, a_n) \geq 0$ where $a_i \in Q$).

Artin solved the problem (the qualitative version) in the affirmative and for this he introduced and with Schreier characterized the real closed fields. A real closed field is a formally real field, which does not allow of any formally real proper algebraic extensions. These real closed fields have the property that any polynomial of odd degree (with coefficients from the real closed field) has a root in it. Moreover the adjunction of square root of -1 gives the algebraic closure of real closed field. In a real closed field, the positive cone is given by the sums of squares of its elements. Artin⁵ proved the following

Theorem 2 Let (K, P) be an ordered field with \hat{K} as its real closure (which exists and is unique up to K -isomorphism). Denote by $K_n = K(x_1, x_2, \dots, x_n)$ the rational function field in n variables over K . Let $f \in K_n$ be such that $f(\alpha) = f(a_1, a_2, \dots, a_n) \geq 0$ in K for all $\alpha \in (a_1, a_2, \dots, a_n) \in K^n$ such that $f(x_1, x_2, \dots, x_n) = \sum_{i=1}^r b_i f_i^2$ for a suitable integer j .

In case P is the only order of K , then b_i is a sum of squares in K for each i . (For instance, K is an Euclidean field or a Pythagorean field).

We will not give a proof of the above theorem. One may find a proof in Jacobson¹ or Lorenz⁶. Artin used Sturm's theorem in counting the real zeros of a polynomial over the real field in a given interval and the theory of formally real fields.

Valuations

The origins of the theory of valuations may be traced to Kummer. It came to prominence with the work of Hensel when he investigated solutions of congruences modulo different powers of a prime p . Other major contributors are Rychlik, Ostrowski, Krull, Hasse, etc. This theory also gained, from an algebraic approach to geometry, especially when one considers the behavior (or properties of an algebraic variety) at a point. Thus the notion of a place from geometry is equivalent to valuations and valuation ring as we see below. We begin with the definition of general valuation as given by Krull. Other (equivalent) definitions are due to Artin² for rank 1 valuations and to Nagata⁸ for general valuations.

Definition 1. A valuation v on a field K is a homomorphism of the multiplicative group K^* of nonzero elements of K to an ordered abelian group Γ with the additional property

$$v(a \pm b) \geq \text{Min } \{v(a), v(b)\}.$$

By setting $v(0) = \infty$, where $\infty > \gamma$ for all γ in Γ and ∞ having the usual properties associated with the symbol, we extend v to K .

The following properties are easy to verify :

- (a) If $D = \{a \in k \mid v(a) \geq 0\}$ then D is a subring of K .
- (b) The set $M = \{a \in k \mid v(a) > 0\}$ is a maximal ideal of D .
- (c) All elements of D not in M are units in D .
- (d) If a, b in K with $v(a) < v(b)$, then $v(a+b) = v(a)$.

The ring D is called the valuation ring of K with respect to the valuation v . It is a local ring with M as its unique maximal ideal. The field D/M is called the residue class field of the valuation v . Here are some examples of fields with valuations.

- (i) Every field K has the trivial valuation namely $v(a) = 0$ for all $a \neq 0$ in K and $v(0) = \infty$.
- (ii) In the field of rational numbers Q , for each prime p , we define $v_p(r) = n$ if p^n divides r exactly

This means writing $r = a/b$ in the lowest terms so that $(a, b) = 1$, p^n divides a exactly and $(p, b) = 1$, or p^n divides b exactly and $(p, a) = 1$ (in case $n < 0$).

(iii) The field of rational numbers Q , real numbers R and complex numbers C have the usual absolute value (i.e. $|a| = a$ if $a \geq 0$ and $-a$ if $a < 0$ for all $a \in Q$ or R and $|a| = \text{positive square root of } N(a) = \text{norm of } a = x^2 + y^2$ if $a \in C$ ($a = x + iy$)). This associates with each element of (Q , R or C) an element of the set of positive real numbers which satisfies the following properties : $|a| \geq 0$ and equality holds if and only if $a = 0$, $|a \cdot b| = |a| \cdot |b|$ and $|a+b| \leq |a| + |b|$. This function arising out of the absolute value is known as the Archimedean valuation. Note that this valuation satisfies a weaker inequality than the one given in the definition and takes the values in the multiplicative group of positive real numbers and zero added to this group.

(iv) In the field of rational functions $K = k(x)$ in one variable x over a field k , each irreducible polynomial $p(x)$ in $k[x]$ gives a valuation (this is given exactly as in example (iii) with the irreducible polynomial playing the role of a prime and a and b are polynomials). Besides these, there is the valuation given by x^{-1} . We now define the notion of a place.

Definition 2 · A place on a field K is a homomorphism φ of a subring K_φ of K into a field k satisfying the following:

- (a) if $a \in K$, $a \notin K_\varphi$ then $a^{-1} \in K_\varphi$ and $\varphi(a^{-1}) = 0$.
- (b) there exists some x in K_φ for which $\varphi(x) \neq 0$.

This notion comes from algebraic geometry. It can be shown that if R is a subring of a field K and A is a proper ideal of R , then there exists a place φ of K such that $K_\varphi \supset R$ and $A \subset M_\varphi = \{a \in K \mid \varphi(a) = 0\}$.

Examples of places :

1. Consider an irreducible element f in a unique factorization domain R . Then the ideal A generated by f is a prime ideal so that R/A is an integral domain. Let K be the field of quotients of R and k the field of quotients of R/A . Then the canonical homomorphism φ of R to R/A can be extended to the subring R_f consisting of all those fractions a/b with a, b in R and $b \notin A$. This extended homomorphism is indeed a place.
2. If Δ is a Dedekind domain, and M is a maximal ideal of Δ then the homomorphism of Δ onto Δ/M can be extended to the local ring $\Delta_M = \{a/b, ab \in \Delta, b \notin M\} \subset K$ the field of fractions of Δ . This extension is again a

place (For more information about places see Zariski-Samuel's Commutative Algebra. (Vol. II, Chapter VI).

We have the notion of a valuation ring, which is defined as follows.

Definition 3 : A valuation ring R of a field K is a subring of K such that of x and x^{-1} ($x \neq 0$) in K , at least one belongs to R .

Examples of valuation rings.

1. Consider the field of rational numbers \mathbb{Q} with the valuation v_p given a prime p . Then

$\mathbb{Z}_p = \{r = a/b \in \mathbb{Q} \mid p \text{ does not divide } b\}$ is a valuation ring.

2. In the field $K = k(x)$ of rational functions in x over k , let $p(x) \in k[x]$ be an irreducible polynomial of degree > 0 . Then $R_p = \{f/g \in K \mid f, g \in k[x] \text{ and } p(x) \text{ does not divide } g(x)\}$ is a valuation ring.
3. Any finite field F has only the trivial valuation. This is clear since any non zero element in F is a root of unity.

We are ready to show that the three notions valuation, place and valuation ring are equivalent.

Let (k, v, Γ) be a field with a valuation with value group Γ (with ∞ added to it). Let $R = \{a \in K \mid v(a) \geq 0\}$. Then R is a ring with identity. If $a \in K$ does not belong to R , then $v(a) < 0$ so that $-v(a) = v(a^{-1}) > 0$ and therefore $a^{-1} \in R$. Thus R is a valuation ring.

Now given a valuation ring R of a field K , consider the ideal M consisting of those a in K which are in R while $a^{-1} \notin R$. This M is a maximal ideal of R . Setting $k = R/M$ and defining a homomorphism φ from K to k by $\varphi(a) = \bar{a}$ as the canonical image of a , in k in case $a \in R$ and $\varphi(a) = \infty$ if $a \notin R$, we see that φ is a place on K .

Finally, given a place φ of K whose image is in the field k , we shall produce an ordered abelian group Γ and a valuation v on K with value group Γ . For this purpose, consider the multiplicative group K^* of non-zero elements of K and the set $U = \varphi^{-1}(k^*)$ the pre image of the non-zero elements of k .

Denote the quotient group K^*/U by Γ the natural homomorphism from K^* to Γ by v . We order this Γ as follows. The positive part Γ_+ of Γ is the image of the set M under

the map v where M is the set of those elements of K^* which are mapped onto 0 by φ . (We shall use the additive notation for the group operation induced by the multiplication in K). As this set M is closed under multiplication the set Γ_+ is closed under addition, that is to say $\Gamma_+ + \Gamma_+ \subseteq \Gamma_+$.

Let $x \in K^* \setminus M$. Then $v(x)$ is not in Γ_+ . If $\alpha \in \Gamma$ there exists an a in K^* such that $v(a) = \alpha$. Should α belong to Γ_+ , then a is in M so that $a^{-1} \notin M$ and $v(a^{-1}) = -v(a) = -\alpha \notin \Gamma_+$. Thus $\Gamma_+ \cap (-\Gamma_+) = \{0\}$. In case $\alpha \in \Gamma_+$ and $\alpha \neq 0$ then $\alpha \notin U$ and $\alpha \notin M$ so that $\alpha^{-1} \in M$ and therefore $-\alpha \in \Gamma_+$ fulfills the conditions for the positive part of a totally ordered group.

To establish that v is a valuation we need to show that $v(a \pm b) \geq \min \{v(a), v(b)\}$.

Suppose $v(a) \geq v(b)$. Then $v(1 + a/b) = v(a+b) - v(b)$ we observe that a/b and therefore also $(a+a/b)$, belong to the pre image of $\Gamma_+ \cup \{\infty\}$ which shows that $v(a+b) = v(a+b) - v(b)$. Thus $v(a+b) \geq \min \{v(a), v(b)\}$. From the way we have obtained v and Γ it is obvious that v is onto. Thus (K^*, v, Γ) is a field with a valuation.

As mentioned earlier, the fields of real and complex numbers have limiting processes due to the presence of the archimedean valuation arising out of the usual absolute value and the usual metric determined by this valuation. In a similar manner the p -adic valuation for different primes p in the field of rational numbers gives rise to ultra metrics (as these metrics satisfy a stronger inequality) which are different for distinct primes. Each of these p -adic topologies results in different limiting processes. Yet, the exceptional position of the topological fields of real and complex numbers is not an accident but a necessity arising out of general considerations. In this connection, the following theorem of Pontrajagin is important.

Theorem 3 : Let K be a locally compact field, which is connected and satisfies the second axiom of countability. Then K is isomorphic to one of the following fields : the field of real numbers, the field of complex numbers or the skew field (in case K is not commutative) of real quaternion.

Quadratic Forms

The history of quadratic forms can be traced to antiquity. For instance, the Greeks knew the Pythagorean triples. The Renaissance came about with the theorem of Lagrange, which says that every natural number (and therefore also every positive rational number) can be expressed as a sum of at most four squares and that there are numbers which require four squares. During the 19th and early 20th century a good

deal of development took place in the arithmetic theory of quadratic forms. For instance, in the first quarter of 20th century, C.L. Siegel developed the arithmetic theory of quadratic forms, which carries over from the field of rational numbers to algebraic number field and much more. Among several applications of his results the thing that is relevant for our discussion is the following. If $f(\theta) = \sum(a_r \cos r\theta + b_r \sin r\theta)$ where r runs from 1 to n , a_r, b_r are real numbers, is non-negative definite (that is to say $f(\theta) \geq 0$ for all values of θ), then $f(\theta)$ has a representation as a sum of squares. In fact, it can be expressed as a sum of eight squares with rational coefficients and trigonometric polynomials in $\theta/2$. In other words,

$$f(\theta) = \sum g_s^2(\theta/2) \text{ where } g_s(\theta/2) = \sum \{c_r^s \cos(r\theta/2) + d_r^s \sin(r\theta/2)\}$$

in which c_r^s, d_r^s are rational numbers, r varies from 1 to n and s varies from 1 to 8.

The above result may be viewed as an extension to trigonometric polynomials of the following theorem of Hilbert² and Landau³ and mentioned in the section on Order.

Theorem 4 : Let K be a field of characteristic different from 2. Then an element a in K is a sum of squares if and only if a is totally positive. Here by totally positive we understand that if K is finite extension of the field of rational numbers then a in K is positive in every real embedding of K and in case K is a finite field then every a is totally positive.

An n -ary quadratic form over a commutative ring R or a field K is a homogeneous polynomial of degree 2 in n -variables. (We assume that 2 is not the characteristic of K) It may be expressed as $f(x_1, \dots, x_n) = \sum a_{ij}x_i x_j$, $1 \leq i, j \leq n$. Since the characteristic of K is not 2, we may replace a_{ij} by $(a_{ij} + a_{ji})/2$ in which case the matrix representing f namely the matrix of coefficients of f is symmetric.

Given an n -ary quadratic form g , we define a quadratic space V over K as an n -dimensional vector space over K with the map (also denoted by) g from V to K satisfying the following properties

- (a) $g(a.v) = a^2.g(v)$ for a in K and v in V .
- (b) The map $b : V \times V \rightarrow K$ given by $b(v_1, v_2) = \frac{1}{2} \{g(v_1 + v_2) - g(v_1) - g(v_2)\}$ is K -bilinear.

Let (V_1, g_1) and (V_2, g_2) be two quadratic spaces over K . We say these are isometric if there exists a K -linear isomorphism T of V_1 to V_2 such that $g_1(v) = g_2(Tv)$

for all v in V_1 . It is not difficult to see that the isometry classes of n -dimensional quadratic spaces over K are in 1-1 correspondence with the equivalence classes of n -ary quadratic forms over K . (By equivalence of two n -ary quadratic forms g_1 and g_2 we mean the following : there exist a nonsingular linear transformation T in $GL(n, K)$ such that $g_1(X) = g_2(TX)$ where X is the row vector (X_1, X_2, \dots, X_n) of the n -variables).

In the late 1930's Witt developed the algebraic theory of quadratic forms by introducing the orthogonal sum and Kronecker (or tensor) product in the collection of equivalence classes of quadratic spaces over K . Thus, if (V_1, g_1) and (V_2, g_2) are two quadratic spaces over K of dimensions n_1 and n_2 respectively, then the quadratic space (V, g) of dimension $(n_1 + n_2)$ is given by $V = V_1 \oplus V_2$ and $g(v) = g(v_1 + v_2) = g(v_1) + g_2(v_2)$ where $v = v_1 + v_2$. If A_i is the symmetric matrix representing g_i for $i = 1, 2$, then the matrix of g is $\begin{pmatrix} A_1 & O \\ O & A_2 \end{pmatrix}$. It can be seen that the orthogonal sum depends only on the equivalence classes of the summands.

If, instead of the direct sum of V_1 and V_2 , we take the tensor product of these two spaces over K namely $V_1 \otimes V_2$ and take the quadratic form g determined by the matrix $A_1 \otimes A_2$, we get (V, \bar{g}) as a quadratic space of dimension n_1, n_2 and this also depends only on the equivalence class. We remark that if g_i is a diagonal form (so that the matrix A_i is a diagonal matrix) then $g = g_1 \otimes g_2$ is given by

$$(a_1 b_1, a_1 b_2, \dots, a_1 b_{n_1}, \dots, a_{n_1} b_1, a_{n_1} b_2, \dots, a_{n_1} b_{n_2})$$

Thus if $g_1 = \langle a_1, \dots, a_{n_1} \rangle$, $g_2 = \langle b_1, b_2, \dots, b_{n_2} \rangle$

then $g = g_1 \perp g_2 = \langle a_1, \dots, a_{n_1}, b_1, b_2, \dots, b_{n_2} \rangle$

and $g_1 \otimes g_2 = \langle \dots, a_i b_j, \dots \rangle \quad 1 \leq i \leq n_1, 1 \leq j \leq n_2$.

The set of equivalence classes of quadratic forms over K forms a cancellative semi ring under the above operations of orthogonal sum and Kronecker product. Here we need Witt's cancellation theorem namely. If g, g_1, g_2 are three quadratic forms over K such that $g \oplus g_1 \cong g_2$ (over K). Here the empty form $g = 0$ of dimension 0 acts as the zero element and the form $1 = \langle 1 \rangle$ of dimension 1 as the unit element. The semi-ring

of equivalence classes of quadratic forms can be extended as a ring and this is the Witt ring of K , and denoted by $W(K)$. (For details one may refer to T.Y. Lam. 191).

Examples of Witt-rings.

- (1) Let $K = R$ be the field of real number. Then the only anisotropic forms over K are 0 , $n \langle 1 \rangle$ and $n \langle -1 \rangle$ where n is any natural number. Thus $W(R) \cong \mathbb{Z}$. Here a quadratic form is said to be anisotropic if it does not represent 0 non-trivially.
- (2) Let K be any field of finite characteristic p . Say $K = \mathbb{Z}/p\mathbb{Z}$ where p is an odd prime. Then we have $W(\mathbb{Z}/p\mathbb{Z}) = (\mathbb{Z}/2\mathbb{Z}) \oplus (\mathbb{Z}/2\mathbb{Z})$ in case $p \equiv 1 \pmod{4}$
and $W(\mathbb{Z}/p\mathbb{Z}) = (\mathbb{Z}/4\mathbb{Z})$ in case $p \equiv 3 \pmod{4}$.
- (3) If K is any algebraically closed field, or K is quadratically closed with characteristic different from 2 so that every element is a square, we have $W(K) = (\mathbb{Z}/2\mathbb{Z})$.
- (4) From (2) above, using Hensel's lemma or otherwise one can show that

$$W(\mathbb{Q}_p) \cong (\mathbb{Z}/2\mathbb{Z})^4 \text{ if } p \equiv 1 \pmod{4}$$

$$\text{and } W(\mathbb{Q}_p) \cong (\mathbb{Z}/4\mathbb{Z})^2 \text{ if } p \equiv 3 \pmod{4}.$$

Relationship between Order and Valuation

In this section we shall investigate the valuations that arise naturally on a field with orderings. We will therefore be interested in orderable fields. Given a formally real field K , there is a natural valuation on K whose residue class field is also a formally real field. This natural valuation is obtained as follows :

As K is formally real, it contains a sub-field isomorphic to the field \mathbb{Q} of rational numbers and also it is orderable. Let P denote the positive cone of some ordering of K .

Set $A(\mathbb{Q}, P) = R = \{a \text{ in } K \mid \text{for some } r \in \mathbb{Q}, r \pm a \in P\}$ and

$$M(\mathbb{Q}, P) = M = \{a \text{ in } K \mid r \pm a \in P \text{ for all } r > 0 \text{ in } \mathbb{Q}\}$$

It can be verified that $A(Q, P)$ is a ring and $M(Q, P)$ is its unique maximal ideal. This ring is the convex hull of Q in K with respect to the chosen ordering P , that is to say if $a < c < b$ and $a, b \in R$ then $c \in R$ (because $r + c = r + a + (c-a)$ belongs to P as $(c-a) \in P$ and $r \pm a \in P$ and $r - c = r - b + b - c$ is in P , since $r \pm b \in P$ and $(b-c) \in P$). Further, the maximal ideal M is also convex in R . For this suppose $0 < a < b$, $b \in M$. Then we have $0 < b^{-1} < a^{-1}$. Since $b \in M$, $b^{-1} \notin R$ and as R is convex, $a^{-1} \notin R$ so that a belongs to M . The residue class field R/M has the induced order with respect to which the positive cone is the canonical image of $P \cap R$ in R/M . Thus the valuation v of K , whose valuation ring is R and residue class field R/M which is an orderable field, is a real valuation arising out of the order P in K . We call this valuation ring $A(Q, P) = R$, the canonical valuation ring of P and the associated valuation v (denoted by v_p to signify that it arises from P) as the canonical valuation.

This canonical valuation v_p is compatible with the ordering P of K in the sense that if $0 < a \leq b$ with respect to the order P , then $v(a) \geq v(b)$.

We have the following :

Theorem 4 : Let P be a given ordering of the field K . Then the family F of all valuation rings in K which are compatible with the ordering P forms a chain under set inclusion. The smallest member is the convex hull of Q with respect to P in K namely, the ring $A(Q, P)$.

In fact, F consists of all sub rings of K which contain $A(Q, P)$.

The residue class field R/M of the canonical valuation v_p of K for the given ordering P is in fact a real valuation. The field R/M with the push down order p (say) is an archimedean ordered field (because for any $x \in R$ since $-r \leq x \leq r$ with respect to the ordering P , for some r in R , by pushing down to R/M we have $-r \leq \bar{x} \leq r$ with respect to the order \bar{P}). Consequently $\{R/M, \bar{P}\}$ has a unique order imbedding into the field of real numbers with its usual ordering.

The above notion of canonical valuation v_p of an ordered field (K, P) is implicit in the paper of Artin-Schreier and Baer and explicit in the paper of Krull¹⁰.

Theorem 5 : Let (K, P) be an ordered field, R its canonical valuation ring for P and v be the canonical valuation. Then the following are equivalent.

- (1) There exists a real valuation ring S contained in the real closure \hat{K} of (K, P) such that $S \cap K = R$

(2) There exists an ordering \bar{P} of the quotient field \bar{K} of the valuation ring $S = A(Q, \bar{P})$ of \bar{K} . This valuation ring is the Henselization of (R, v) and $\hat{P} \cap K = P$.

Given a real field K , we can consider the set X_K of all orderings in K . This set is clearly non-empty as the pre-ordering (which may turn out to be an ordering) arising out of the sums of squares can be expanded to a positive cone of K . We can make X_K into a topological space by using the "Harrison Sets"

$$H(a) = \{P \in X \mid a \in X_K\} \text{ for any } a \in K, a \neq 0,$$

as a sub basis. With this topology X_K becomes a compact Hausdorff space and this is also totally disconnected. This topological space of orderings of a field and its ring theoretic analogue are used in the study of real algebraic geometry.

Suppose now we have an orderable field K that has a valuation v . We may consider X_K^v of the orderings of K , which are compatible with the valuation v . The natural question is what possible relationships can exist between X_K^v and the value group Γ of v ?

Note that if a in K is a square, say $a = b^2$, then $v(a) = 2v(b)$ so that $v(a) \in 2\mathbb{Z}$ (which by abuse of notation we write as Γ^2). We then get a mapping \bar{v} from $K^*/(K^*)^2$ to Γ/Γ^2 . If we take v to be onto, the \bar{v} has a cross section. Thus there exists a map μ from $\Gamma/\Gamma^2 \rightarrow K^*/(K^*)^2$ such that $v \circ \mu = \text{identity}$.

The theorem we state below without proof gives a relationship between X_K^v and Γ .

Theorem 6. Let K be an orderable field with valuation v and value group Γ . Then there is a 1-1 correspondence between the space X_K^v of orderings of K that are compatible with the valuation v and the set $\left(\Gamma/\Gamma^2\right) \times X_k$ where $\left(\Gamma/\Gamma^2\right) = \text{Hom}\left(\Gamma/\Gamma^2, \{\pm 1\}\right)$ and X_k is the space of all orderings of the residue class field k of K with respect to the valuation v .

An immediate corollary of the above is the following result.

If the value group Γ is the 2-divisible so that $\Gamma = \Gamma^2$, then every ordering of k has a unique lifting to an order of K which is compatible with v .

Without the above restriction on Γ , we see that each ordering of k has as many lifting as the index of Γ^2 in Γ to orderings in K which are compatible with v .

Relationship between valuations and quadratic forms :

We begin this section with the well-known local global principle for quadratic forms known also as Hasse-Minkowski theorem.

Theorem 7. Let K be a global field of characteristic different from 2. Let $f(x_1, \dots, x_n)$ be an n -dimensional quadratic form over K . Then f represents zero non-trivially over K if and only if, f represents zero nontrivially over all completions K_p where p is non-archimedean or real.

The above theorem, also known as Hasse-Minkowski's local global principle can be stated as follows : two quadratic forms g_1 and g_2 over a global field K are equivalent if and only if, they are equivalent over K_p for all prime ideals p including the infinite primes. Here K_p denotes the completion of K with respect to the valuation arising out of the prime p .

We will now record some results connecting complete discrete valuation rings and their Witt rings. Let R be a discrete valuation ring with maximal ideal M and residue class field $R/M = k$. We shall assume that 2 is a unit in R . Then in case R is complete under this discrete valuation, R is 2-Henselian. This means that α in R is a square if its residue modulo M in k is a square.

The following result due to Springer are interesting and important.

Theorem 8 : Let R be a 2-Henselian discrete valuation ring in which 2 is a unit. Denote by k the residue class field R/M . Then the canonical surjection of R onto k induces canonical isomorphism of their Witt rings. namely, $W(R) \cong W(k)$. If K is the field of fractions of R , then $W(K) \cong W(k) \oplus W(k)$ and there exists a ring isomorphism of $W(K)$ with $W(k)[T]/(T^2-1)$.

Relationship between Quadratic Forms and Ordered Fields

Let (K, P) be an ordered field and (V, q) be a quadratic space over K . We say (V, q) is positive definite if $q(x) > 0$ for all $x \in V$, $x \neq 0$, and negative definite if $q(x) < 0$ for all non-zero $x \in V$, where the ordering is that induced by the positive cone P in K . Now given a quadratic space (V, q) over (K, P) , we can decompose V as an orthogonal sum $V^+ \oplus V^-$ where V^+ and V^- are such that V^+ with q restricted to it, is positive definite and V^- with q restricted to it, is negative definite. (This orthogonal decomposition is independent of the choice of q from its equivalence class). The dimension of V^+ and V^- are independent of the choice of orthogonal decomposition of q and the dim. $V^+ - \dim. V^-$ is called the signature of the quadratic form q and this is an invariant of q .

The above result is the famous theorem of Jacobi and Sylvester and is known as Inertia theorem. Now using diagonalization of quadratic forms, it is easy to see that if φ and ψ are two quadratic forms over (K, P) , then $\text{sgn}(\varphi \perp \psi) = \text{Signature of the orthogonal sum of } \varphi \text{ and } \psi = \text{sgn}(\varphi) + \text{sgn}(\psi)$ and $\text{sgn}(\varphi \otimes \psi) = \text{sgn}(\varphi) \text{ sgn}(\psi)$

Further, signature of the 1-dimensional form represented by $q(a) = a^2$ for all $a \in K$, $a \neq 0$ is 1 and of the 0-form is 0. Thus this signature gives rise to a homomorphism of the Witt ring of K to the ring Z of integers.

Suppose (K, P) is an Euclidean field so that every sum of squares is itself a square. Then $W(K)$ is isomorphic to Z and K^* has exactly two square classes. In fact, for any formally real field K , the additive group of its Witt ring $W(K)$ is not a torsion group (and this trivially implies that $W(K)$ is not a 2-torsion group).

As in the case of global fields where we have the local global principle of Hasse-Minkowski, for formally real fields we have Pfister's principle. We state this as the following.

Theorem 9: Let K be a formally real field. Then an element q in $W(K)$ is a torsion element if and only if signature of q is zero for every ordering $P \in X(K)$ - the space of all orderings of K .

If q is a torsion element of $W(K)$ then its order is a power of 2.

The above result may be stated differently. Let $P \in X(K)$ and K_p denote the real closure of K with respect to P . The inclusion of K in K_p induces a homomorphism of $W(K)$ in $W(K_p)$ and K_p being real closed we have $W(K_p) \cong Z$ under the signature map. Defining ρ from $W(K)$ to $\pi W(K_p)$ where the product is taken overall P in $X(K)$, we get

a (group) homomorphism and kernel of ρ is the 2-torsion part of $W(K)$. The kernel of ρ considered as a ring homomorphism is in fact the nil radical of $W(K)$. It is also the Jacobson radical of $W(K)$. Thus we have $W(K) =$ torsion subgroup of $W(K)$ is equal to the Jacobson radical of $W(K)$ which is the intersection of all maximal ideals of $W(K)$ and it is also equal to the nil radical of $W(K)$. (Nil radical is the intersection of all prime ideals of $W(K)$).

We have an immediate corollary from the above. If K is not formally real, then $X(K)$ is empty so that the homomorphism $\rho : W(K) \rightarrow \pi W(K_p) = 0$ as ρ runs over an empty set. Thus $W(K)$ is a 2-primary group.

We have a complete description of all orderings of an orderable field K via the prime ideals of the Witt ring of K .

First we start with a :

Definition 4 · Let P be a prime ideal of the Witt ring $W(K)$ of a field K . We define the characteristic of P as the characteristic of the quotient field of $W(K)/P$.

The ideal $I(K)$ of even dimensional quadratic forms over K is the unique prime ideal of characteristic 2. Here is a complete description of all the prime ideals of $W(K)$.

Theorem 10 : (Leicht-Lorenz¹¹, and Harrison). There is a one-to-one correspondence between the set $X(K)$ of all orderings of K and the set of all prime ideals P of $W(K)$ such that $W(K)/P$ is isomorphic to \mathbb{Z} .

One way is easy. Thus if P is an ordering of K , then the ideal arising out of the signature mapping P_p from $W(K) \rightarrow \mathbb{Z}$ is indeed a prime ideal. For the converse, let P be a prime ideal of $W(K)$ such that the ideals $S_{\alpha,p}$ which is the kernel of the composition map $W(K) \rightarrow W(K_p) \rightarrow \mathbb{Z}/p\mathbb{Z}$ where K_p is the real closure of K with respect to p .

All these ideals are different—The prime ideals described by the above theorem are in fact the minimal prime ideals whereas the prime ideals of finite characteristic are the maximal prime ideals.

We shall conclude our discussion with pre-orderings, variations that are compatible with pre-order and Witt rings.

Let T be a pre-order on the field K and X_T denote the set of all orderings P of K , which contain T . This set X_T is a closed subset of the Boolean space $X(K)$ and hence X_T is itself a Boolean space. We have a mapping from the Witt ring of K to the ring $C\{X(K), Z\}$ of integer valued continuous functions from $X(K)$ to Z and from the Witt ring $W_T(K)$ of K relative to the pre-ordering T . This ring $W_T(K)$ is isomorphic to the quotient of $W(K)$ by the ideal generated by the forms $\langle 1, -t \rangle$ as t ranges over the non zero elements of T . Here by $\langle 1, -t \rangle$ we mean the quadratic form $(x_1^2 - tx_2^2)$. In other words, we have $W_T(K) \cong W(K)/\sum W(K) \cdot \langle 1, -t \rangle, t \in T$. There is an imbedding theorem (due to Dubois) from $W(K)$ to $C\{X(K), Z\}$ where $X(K)$ is the Boolean space with the Harrison topology. The kernel of the map is the nil radical. For instance, if for K we take a formally real field and for T the pre-order given by sums of squares of elements ($\neq 0$) of K then the kernel of the homomorphism from $W(K)$ to $C\{X(K), Z\}$ is exactly the ideal in $W(K)$ generated by the forms $\langle 1, -a \rangle$ as a range over sums of non zero squares of K . This kernel is in fact, the torsion subgroup of $W_T(K)$. The quotient ring $W_1(K) \cong WK/W_TK$ for the case $T = \text{sum of squares of } K^*$ is called the reduced Witt ring K .

We have considered the compatibility of order and valuation on a field K . Likewise, we can talk of compatibility of pre-order and valuation. We call a valuation v on a field K to be compatible with a pre-ordering T if v is compatible with some ordering P of K with $P \supseteq T$. If this holds for all P in X_T , we say v is fully compatible with T . We set R_T to be the intersection of all valuation rings of K that are compatible with the pre-order T . Then $R_T = \bigcap R(P)$ where the intersection is taken over all orderings P in X_T . For instance, if we take for T the sums of squares of non zero elements of K , then R_T is the real holomorphy ring which is the intersection of the convex hull of the field of rational numbers with respect to all the orderings of K .

We can associate another sub ring R^1 of K with each pre-order, namely the sub ring generated by the valuation rings $R(P)$ associated with all the orderings P in X_T . This R^1 is indeed a valuation ring (being the over ring of valuation rings) and the valuation associated with this is the finest valuation of K which is fully compatible with the pre-ordering T . For more details and connections with ordered fields, etc., we refer the reader to the beautiful exposition of Lam¹¹.

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A note on the degree of approximation by Taylor means

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Abstract

Two theorems are obtained to measure the degree of approximation from the Taylor transform and several other results including the result of Mohapatra and Chandra have been obtained.

(Keywords . Taylor sums/Hölder metric/degree of approximation)

Introduction

Let $C_{2\pi}$ be the space of all 2π -periodic continuous functions f on $[0, 2\pi]$ with Fourier series :

$$f \sim \frac{a_0}{2} + \sum_{n=1}^{\infty} (a_n \cos nx + b_n \sin nx), \quad (1)$$

Singh^{1,2} defined the space H_{ω} by

$$H_{\omega} = \{f \in C_{2\pi} : |f(x) - f(y)| \leq K \omega(|x-y|)\} \quad (2)$$

and the norm $\| \cdot \|_{\omega*}$ by

$$\|f\|_{\omega*} = \|f\|_c + \sup_{x,y} \Delta^{\omega*} f(x,y) \quad (3)$$

where

$$\|f\|_c = \sup_{0 \leq x \leq 2\pi} |f(x)|, \quad (4)$$

$$\Delta^{\omega*} f(x, y) = \frac{|f(x) - f(y)|}{\omega^*(|x - y|)}, \quad (x \neq y) \quad (5)$$

and $\Delta^0 f(x, y) = 0$. $\omega(t)$ and $\omega^*(t)$ are increasing functions of t . If $\omega(|x - y|) \leq A|x - y|^\alpha$ and $\omega^*(|x - y|) \leq K|x - y|^\beta$, $0 \leq \beta < \alpha \leq 1$; A and K being positive constants, then the space H_α is given by :

$$H_\alpha = \{f \in C_{2\pi} : |f(x) - f(y)| \leq K|x - y|^\alpha, 0 < \alpha \leq 1\} \quad (6)$$

Let $\{S_n\}$ be a sequence of partial sums of the given series $\sum_{n=0}^{\infty} c_n$, where $S_n = c_0 + c_1 + \dots + c_n$, then Taylor means of the sequence (S_n) given by Hardy³, are

$$T_n = \sum_{k=0}^n a_{nk} S_k, \quad (n = 0, 1, 2, \dots). \quad (7)$$

If (a_{nk}) is given by

$$\frac{(1-r)^{n+1} \theta^n}{(1-r\theta)^{n+1}} = \sum_{k=0}^{\infty} a_{nk} \theta^k \quad (0 < r < 1, |r\theta| < 1), \quad (8)$$

then the matrix T_n is called the Taylor matrix.

Miracle⁴ studied the Gibbs phenomena for Taylor means of Fourier series and Forbes⁵ studied the Lebesgue constants for regular Taylor sums. Prössdorf⁶ structured several interesting theorems on the degree of approximation defining the Hölder metric. Chandra and Mohapatra⁷ studied some very interesting results, which include

the results of Prössdorf. Singh^{1,2} gave very general conditions to study the problems on approximation in generalized Holder metric. In this note, we take the definition of generalized Holder metric as given by Singh^{1,2} and try to generalize the following theorem of Mohapatra and Chandra⁷ for Taylor operators.

Theorem Let $0 \leq \beta < \alpha \leq 1$, then for $f \in H_\alpha$,

$$\|T_n(f) - f\|_\beta = O\left[n^{-1/2(\alpha-\beta)}(\log n)^{\beta/\alpha}\right], \quad (9)$$

where $T_n(f, x)$ is the Taylor mean.

Main Results

Theorem 1: Let $\omega(t)$ defined in (2) be such that $\omega(t)/t$ is increasing and $\omega(t)/t^2$ is decreasing. For $0 < r \leq 1/2$ and $0 \leq \beta < \eta \leq 1$, we have

$$\|T_n(f; x) - f(x)\|_{\omega*} = O\left[\left\{\omega\left(\pi/n^r\right)\right\}^{1-\frac{\beta}{\eta}} \left\{(\log n)^{\beta/\eta} + n^{2r-1}\right\}\right]. \quad (10)$$

Theorem 2: Let $\omega(t)$ defined in (2) be such that

$$\int_t^\pi u^{-2}\omega(u)du = O\{H(t)\}, \quad (11)$$

where $H(t) \geq 0$ be such that

$$\int_0^t H(u)du = O\{H(t)\}, \quad t \rightarrow 0^+. \quad (12)$$

Then, for $0 < r \leq 1/2$, $0 \leq \beta < \eta \leq 1$ and $f \in H_\omega$, we have

$$\|T_n(f; x) - f(x)\|_{\omega} = O\left[\left\{H\left(\pi/n^r\right)\right\}^{1-\frac{\beta}{\eta}} \left\{ \left(n^{-r}\right)^{1-\frac{\beta}{\eta}} (\log n)^{\beta/\eta} + n^{2r-1} \right\}\right]. \quad (13)$$

To prove above theorems, we shall require the following :

Lemma 1 (Forbes⁵) : For $0 < r < 1$, $|r\theta| < 1$, $0 \leq t \leq \pi$ and h , given by

$$1-re^u = he^u, \quad \theta = \tan^{-1}\left(\frac{r \sin t}{1-r \cos t}\right), \quad (14)$$

we have

$$\{(1-r)/h\}^n \leq \exp(-knt^2), \quad k = \frac{r}{2(1-r)^2} \quad (15)$$

and

$$\left[\{(1-r)/h\}^n - \exp\left(\frac{-nrt^2}{2(1-r)^2}\right) \right] = O(nt^4). \quad (16)$$

Lemma 2 (Miracle⁴) : Let $r > 0$ and θ be as given in Lemma 1, then for some constant K , we have

$$\left\{ \theta - \frac{rt}{1-r} \right\} \leq Kt^3, \quad (0 \leq t \leq \pi/2). \quad (17)$$

Lemma 3 : Let

$$\phi_x(t) = f(x+t) + f(x-t) - 2f(x), \quad (18)$$

where $f \in H_\omega$, then

$$|\phi_x(t) - \phi_y(t)| \leq 4\omega(|x - y|) \quad (19)$$

and

$$|\phi_x(t) - \phi_y(t)| \leq 4\omega(|t|). \quad (20)$$

We shall use the following notations used by Mohapatra and Chandra⁷, as

$$L(n, r, t, \theta) = \sum_{k=0}^{\infty} a_{nk} \sin(n+1/2)t \quad (21)$$

and

$$L(n, r, t, \theta) = \left[\left\{ (1-r)/h \right\}^{n+1} \sin \left\{ (n+1/2)t + (n+1)\theta \right\} \right], \quad (22)$$

for $0 < r < 1$, $|r\theta| < 1$ and $(1-r e^{it}) = h e^{-i\theta}$, $0 \leq t \leq \pi$. For completeness, we give the proof of (22).

Using

$$\sum_{k=0}^{\infty} a_{nk} \phi^k = \frac{(1-r)^{n+1} \phi^n}{(1-r\phi)^{n+1}},$$

we have

$$\begin{aligned} \sum_{k=0}^{\infty} a_{nk} \sin(k+1/2)t &= \operatorname{Im} \sum_{k=0}^{\infty} a_{nk} e^{(k+1/2)it} \\ &= \operatorname{Im} \left(e^{it/2} \sum_{k=0}^{\infty} a_{nk} \phi^k \right), \quad \phi = e^{it} \\ &= \operatorname{Im} e^{it/2} \frac{(1-r)^{n+1} e^{mt}}{(1-r e^{it})^{n+1}} \end{aligned}$$

$$\begin{aligned}
&= \operatorname{Im} e^{(n+1/2)it} \frac{(1-r)^{n+1}}{(he^{-i\theta})^{n+1}}, \quad 1-re^{it} = he^{-i\theta} \\
&= \{(1-r)/h\}^{n+1} \operatorname{Im} \exp[\{(n+1/2) t + (n+1)\theta\} i] \\
&= \{(1-r)/h\}^{n+1} \sin \{(n+1/2) t + (n+1)\theta\}.
\end{aligned}$$

Proof of Theorem 1:

Following Zygmund⁸, we have

$$T_n(f;x) = \sum_{k=0}^{\infty} a_{nk} s_k(x).$$

We write

$$l_n(x) = T_n(f;x) - f(x) = \frac{1}{\pi} \int_0^{\pi} \frac{\phi_x(t)}{\sin t/2} L(n, r, t, \theta) dt \quad (23)$$

where $L(n, r, t, \theta)$ is given in (22)

$$\begin{aligned}
|l_n(x) - l_n(y)| &\leq \int_0^{\pi} \frac{|\phi_x(t) - \phi_y(t)|}{\sin t/2} |L(n, r, t, \theta)| dt \\
&= \left(\int_0^{\pi/n} + \int_{\pi/n}^{\pi} \right) |L(n, r, t, \theta)| dt \\
&= I_1 + I_2. \quad (24)
\end{aligned}$$

Since $|1-r| \leq h$, we have by (20) and (22)

$$\begin{aligned}
I_1 &= O(1) \int_0^{\pi/n} \frac{\omega(|t|)}{t} dt \\
&= O\{\omega(\pi/n)\}. \tag{25}
\end{aligned}$$

By Lemma 3, (22) and (15), we have

$$\begin{aligned}
I_2 &= O(1) \int_{\pi/n}^{\pi} \frac{\omega(|t|)}{t} \exp(-knt^2) dt \\
&= O(1/n) \int_{\pi/n}^{\pi} \frac{\omega(t)}{t^2} \frac{d}{dt} \{\exp(-knt^2)\} dt \\
&= O\{n^{2r-1} \omega(\pi/n)\}. \tag{26}
\end{aligned}$$

Next, we estimate I_1 and I_2 , using (19) instead of (20), we find that

$$I_1 = I_{11} + I_{12}. \tag{27}$$

Since $|1-r| \leq h$ and $\sin \theta \leq \theta$ for $0 \leq t \leq \pi/n$ and keeping in view lemma 2

$$\begin{aligned}
I_{11} &= O\left[\omega(|x-y|) \int_0^{\pi/n} \frac{1}{t} \left\{ (n+1/2)t + (n+1) \left(kt^3 + \frac{rt}{1-r} \right) \right\} dt \right] \\
&= O\left[\omega(|x-y|) O(n) \int_0^{\pi/n} \left(1 + kt^2 + r/(1-r) \right) dt \right]
\end{aligned}$$

$$I_{11} = O[\omega(|x-y|)],$$

since $t^3 \leq t$ for $0 \leq t \leq \pi/n$ and n is large.

Further

$$I_{12} = O \left[\omega(|x - y|) \int_{\pi/n}^{\pi/n'} (1/t) |L(n, r, t, \theta)| dt \right],$$

Since $|\sin \{(n+1/2)t + (n+1)\theta\}| \leq 1$ and $|1-r| \leq h$, owing to (22)

$$\begin{aligned} I_{12} &= O \left[\omega(|x - y|) \int_{\pi/n}^{\pi/n'} \frac{1}{t} dt \right] \\ &= O \left[\omega(|x - y|) \log n \right], \end{aligned} \quad (29)$$

then

$$I_1 = O \left[\omega(|x - y|) \log n \right]. \quad (30)$$

Since, $\{(1-r)/h\}^n \leq \exp(-knt^2)$ for $0 \leq t \leq \pi$

$$\begin{aligned} I_2 &= O \left[\omega(|x - y|) \int_{\pi/n'}^{\pi} \frac{1}{t} L(n, r, t, \theta) dt \right] \\ &= O \left[\omega(|x - y|) \frac{1}{n} \int_{\pi/n'}^{\pi} t^{-2} \frac{d}{dt} \{ \exp(-knt^2) \} dt \right] \\ &= O \left[\omega(|x - y|) n^{2r-1} \right] \end{aligned} \quad (31)$$

Now using

$$I_k = I_k^{1-\beta/\eta} I_k^{\beta/\eta} \quad (32)$$

we have

$$I_1 = O \left[\left\{ \omega \left(\pi / n^r \right) \right\}^{1-\beta/\eta} \left\{ \omega(|x-y|) \log n \right\}^{\beta/\eta} \right] \quad (33)$$

and

$$I_2 = O \left[\left\{ n^{2r-1} \omega \left(\pi / n^r \right) \right\}^{1-\beta/\eta} \left\{ n^{2r-1} \omega(|x-y|) \right\}^{\beta/\eta} \right]. \quad (34)$$

Thus

$$\begin{aligned} \sup_{x,y} \left\{ \Delta^{\omega*} 1_n(x, y) \right\} &= \sup_{x,y} \frac{|1_n(x) - 1_n(y)|}{\omega^*(|x-y|)} \\ &= O \left[\left\{ \omega \left(\pi / n^r \right) \right\}^{1-\beta/\eta} \left\{ (\log n)^{\beta/\eta} + n^{2r-1} \right\} \right], \end{aligned} \quad (35)$$

$$\|1_n\|_c = \max_{0 \leq x \leq 2\pi} |T_n^r(f; x) - f(x)| = O \left[n^{2r-1} \omega(|x-y|) \right] \quad (36)$$

Combining above results, we get

$$\|T_n^r(f; x) - f(x)\|_{\omega*} = O \left[\left\{ \omega \left(\pi / n^r \right) \right\}^{1-\beta/\eta} \left\{ (\log n)^{\beta/\eta} + n^{2r-1} \right\} \right]. \quad (37)$$

This completes the proof of theorem 1.

Proof of Theorem 2 follows analogously as the proof of Theorem 1 with slight changes, so we omit details.

Corollary:

Let $r = 1/2$ and $\eta = \alpha$ in Theorem 1, and $\omega(t)$ be as given in (2) such that $\omega(t)/t$ is increasing and $\omega(t)/t^2$ is decreasing, then we have

$$\left\| T_n'(f; x) - f(x) \right\|_{\omega_*} = O \left[\left\{ \omega \left(\pi / n^{1/2} \right) \right\}^{1-\beta/\alpha} (\log n)^{\beta/\alpha} \right] \quad (38)$$

for $0 \leq \beta < \alpha \leq 1$.

Deduction 1 : If we put $\omega(t) = O(t^\alpha)$, $0 < \alpha \leq 1$ and $0 < \beta < \alpha \leq 1$, in the above corollary, then the theorem of Mohapatra and Chandra⁷ follows.

Deduction 2 : Again, putting $\beta = 0$, $\omega(t) = O(t^\alpha)$, $r = \frac{1}{2}$, we get

$$\left\| T_n'(f; x) - f(x) \right\| = O(n^{-(1/2)\alpha}). \quad (39)$$

Deduction 3 : If we put $H(t) = t^{\alpha-1}$, $0 < \alpha < 1$ and $0 \leq \beta < \alpha < 1$, then

$$\left\| T_n'(f; x) - f(x) \right\| = O \left[n^{-r(\alpha-\beta)} (\log n)^{\beta/\alpha} \right] \quad (40)$$

and if $H(t) = \log(\pi/t)$, $\alpha = 1$, $0 < r < 1/2$ we get

$$\left\| T_n'(f; x) - f(x) \right\| = O \left[(\log n^r)^{1-\beta} \left\{ (n^{-r})^{1-\beta} (\log n)^\beta + n^{2r-1} \right\} \right]. \quad (41)$$

Deduction 4 : If we put $\beta = 0$ in above deduction, we get

$$\left\| T_n'(f; x) - f(x) \right\| = O \left[n^{-r\alpha} \right], \quad 0 < \alpha < 1 \quad (42)$$

and

$$\left\| T_n'(f; x) - f(x) \right\| = O \left[\left(\frac{\log n^r}{n^r} \right) \right], \quad \alpha = 1, \quad 0 < r \leq 1/3.$$

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Effect of perturbation in Coriolis and centrifugal forces in the location of libration point in a new kind of 3-body problem

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Abstract

The effect of small perturbation in the Coriolis and centrifugal forces on the location of libration point in a new kind of 3-body problem, has been studied when $0 < K < 1$.

(Keywords : 3-body problem/perturbation/Coriolis force/centrifugal force).

Introduction

A new kind of 3-body problem has been considered by Robe¹, in which one body, M_1 is a rigid spherical shell filled with a homogeneous incompressible fluid of density ρ_1 . The second one, M_2 is a mass point outside the shell and M_3 is a small solid sphere of density ρ_3 supposed to be moving inside the shell. The problem constitutes a model for the motion of an artificial earth satellite M_3 inside another one M_1 , M_2 being the earth. M_3 is assumed to be infinitesimal. Mass of the three bodies are m_1 , m_2 and m_3 respectively.

There are three forces acting on M_3 —

- (i) The attraction of M_2
- (ii) The gravitational force F_A exerted by the fluid of density ρ

$$F_A = (4/3) \pi G \rho_1 m_3 M_1 M_3$$

where $M_1 M_3$ denote the distance of centres of the first and third body

(iii) The buoyancy force $F_B = (4/3)\pi G \rho_1^2 m_3 M_1 M_2 / \rho_3$

The total potential action at m_3 is

$$\begin{aligned} & -Gm_2/r_2 + (4/3)\pi G \rho_1 \{1 - (\rho_1/\rho_3)\} r_1^2/2 \\ & = -Gm_2/r_2 + Kr_1^2/2 \end{aligned}$$

where $r_1 = M_1 M_3$, $r_2 = M_2 M_3$, $K = 4/3 \pi \rho_1 (1 - \rho_1/\rho_3)$

and G is assumed to be unity.

Shrivastava and Garain² used the small perturbation ϵ and ϵ' in Coriolis and centrifugal forces in the above problem. They considered M_3 to be infinitesimal, the orbit to be circular and $\rho_1 = \rho_3$ i.e. $K = 0$ and obtained the equilibrium point $[-\mu + \epsilon'\mu/(1+2\mu), 0, 0]$. Shrivastava and Garain³ also studied the stability of libration point under the same assumption. They found that the range of stability increases for the point lying in one part and decreases for the point lying on the other part of the straight line $-250\epsilon + 129\epsilon' = 0$.

Here we shall apply the small perturbation in Coriolis and centrifugal forces in Robe's¹ problem. We consider the orbit to be circular, $\rho_1 \neq \rho_3$ and $0 < K < 1$.

The Location of Libration Point

The equation of motion in Synodic system of co-ordinate are

$$\ddot{x} - 2\dot{y} - x = \partial v / \partial x$$

$$\ddot{y} + 2\dot{x} - y = \partial v / \partial y$$

$$\ddot{z} = \partial v / \partial z \quad (1)$$

where $\nu = \mu/[(x_2 - x)^2 + y^2 + z^2]^{1/2} - (k/2) [(x - x_1)^2 + y^2 + z^2]$,

$\mu = m_2/(m_1 + m_2)$, $x_1 = -\mu$, $x_2 = 1 - \mu$, $0 < \mu < 1$.

For unit of mass, we consider $m_1 + m_2 = 1$ and for the unit of distance, the distance between centre of M_1 and $M_2 = 1$.

$$\therefore 0 < (4/3)\pi \rho_1 = (4/3)\pi \rho_1 / (m_1 + m_2) < (4/3)\pi \rho_1 \dots$$

$$= (4/3)\pi \rho_1 / [(4/3)\pi r^3 \rho_1], \quad (r \text{ be the radius of } M_1)$$

$$= 1/r^3$$

$$\therefore 0 < (4/3)\pi \rho_1 (1 - \rho_1/\rho_3) < (1/r^3) (1 - \rho_1/\rho_3)$$

$$(\rho_3 - \rho_1) / (r^3 \rho_3)$$

$$\therefore 0 < K < (\rho_3 - \rho_1) / (r^3 \rho_3)$$

let $(\rho_3 - \rho_1) / (r^3 \rho_3) < 1$

i.e. $\rho_3 - \rho_1 < r^3 \rho_3$

$$\Rightarrow \rho_3 (1 - r^3) < \rho_1$$

then $0 < K < 1$.

Now we consider the perturbation in Coriolis and centrifugal forces with the help of parameter α and β , the unperturbed value of both being unity. Thus we may write the eqn. (1) in the form

$$\ddot{x} - 2\alpha \dot{y} - \beta x = \partial \nu / \partial x$$

$$\ddot{y} + 2\alpha \dot{x} - \beta y = \partial \nu / \partial y$$

$$\ddot{z} = \partial v / \partial z \quad (2)$$

where $\alpha = 1 + \varepsilon$, $|\varepsilon| < < 1$

$$\beta = 1 + \varepsilon', |\varepsilon'| < < 1$$

This equation (2) is written as

$$\ddot{x} - 2\alpha\dot{y} = \partial\Omega / \partial x$$

$$\ddot{y} + 2\alpha\dot{x} = \partial\Omega / \partial y$$

$$\ddot{z} = \partial\Omega / \partial z \quad (3)$$

$$\text{where } \Omega = (\beta/2) (x^2 + y^2) - ((k/2) [x - x_1]^2 + y^2 + z^2) + \mu / [(x^2 - x)^2 + y^2 + z^2]^{1/2}$$

From eqn (3), we get the Jacobi integral

$$0 = \dot{x}^2 + \dot{y}^2 + \dot{z}^2 - 2\Omega + c \equiv \psi(x, y, z, \dot{x}, \dot{y}, \dot{z})$$

Libration points are obtained by assuming

$$\psi_x = \psi_y = \psi_z$$

$$\text{i.e. } \Omega_x = \Omega_y = \Omega_z = 0$$

$$\Omega_x = \beta x + \mu(1 - \mu - x) / [(1 - \mu - x)^2 + y^2 + z^2]^{3/2} - k(x + \mu) = 0 \quad (4)$$

$$\Omega_y = \beta y - \mu y / [(1 - \mu - x)^2 + y^2 + z^2]^{3/2} - ky = 0 \quad (5)$$

$$\Omega_z = [\mu / \{(1 - \mu - x)^2 + y^2 + z^2\}^{3/2} + k] z = 0 \quad (6)$$

From eqn (6), we get that

$$[\mu / (1-\mu - x)^2 + y^2 + z^2]^{3/2} + k \neq 0$$

$$\therefore z = 0.$$

Putting $y = 0, z = 0$ in eqn. (4), we have

$$\beta x + \mu / (1-\mu - x)^2 - k(x + \mu) = 0 = f(x) \text{ (say)} \quad (7)$$

$$f(-\mu) = \mu(1-\beta) < 0 \quad (\because \beta > 1)$$

$$f(0) = \mu[1/(1-\mu)^2 - k] > 0$$

$$\because 0 < 1 - \mu < 1 \text{ and } 0 < k < 1$$

$$\Rightarrow 1/(1-\mu) > 1$$

$$\Rightarrow 1/(1-\mu)^2 > 1$$

$$\therefore 1/(1-\mu)^2 - k > 0.$$

Hence one root of the equation lies between $-\mu$ and 0.

Now, we consider that $x = -\mu + \rho$

\therefore Eqn (7) reduces to

$$\beta(\rho - \mu) + \mu / (1 - \mu + \mu - \rho)^2 - k(\rho - \mu - \mu) = 0$$

$$\Rightarrow \rho^3 (\beta - k) + \rho^2 (-2\beta - \mu\beta + 2k) + \rho (2\mu\beta + \beta - k) + \mu - \mu\beta = 0 \quad (8)$$

Now, we use the small parameter method to find the value of ρ from eqn. (8) by putting $\mu = 0$.

∴ we have $(\beta - k) \rho(\rho^2 - 2\rho + 1) = 0$

∴ either $\beta - k = 0$ or $\rho = 0$ or $\rho^2 - 2\rho + 1 = 0$

If $\beta - k = 0$, then $\beta = k$, which is impossible.

If $\rho^2 - 2\rho + 1 = 0$, then $\rho = 1$, which is also impossible.

So, $\rho = 0(\mu) = c_1\mu + c_2\mu^2 + c_3\mu^3 + \dots$

Putting this value of ρ in eqn (8), we have

$$(\beta - k) \{c_1^3\mu^3 + 3c_1^2c_2\mu^4 + 3(c_1^2 + c_3 + c_1c_2^2)\mu^5 + \dots\}$$

$$+ (-2\beta - \mu\beta + 2k) \{c_1^2\mu^2 + 2c_1c_2\mu^3 + (c_1c_3 + c_2)\mu^4\}$$

$$+ (2\mu\beta + \beta - k) (c_1\mu + c_2\mu^2 + c_3\mu^3 + \dots) + \mu - \mu\beta = 0$$

Equating the co-efficient in the same power of μ to be zero, we get

$$1 - \beta + c_1(\beta - k) = 0$$

$$\Rightarrow c_1 = (\beta - 1) / (\beta - k) = \varepsilon' / (\beta - k)$$

$$c_2(\beta - k) + 2c_1\beta - c_1^2(2\beta + 2k)$$

$$\Rightarrow c_2 = (-2\varepsilon') / (\beta - k)^2 \text{ (neglecting the higher power of } \varepsilon')$$

$$2\beta c_2 + c_3(\beta - k) = 0$$

$$\Rightarrow c_3 = 4\varepsilon' / (\beta - k)^3 \dots$$

$$\begin{aligned}
 & \rho \varepsilon' \mu / (\beta - k) - (2 \varepsilon' \mu^2) / (\beta - k)^2 + (4 \varepsilon' \mu^3) / (\beta - k)^3 + \dots \dots \dots \\
 &= \varepsilon' \mu / (\beta - k) [1 - 2\mu / (\beta - k) + (2\mu)^2 / (\beta - k)^2 + \dots \dots \dots] \\
 &= [\varepsilon' \mu / (\beta - k)] [1 + 2\mu / (\beta - k)]^{-1} \\
 &= \varepsilon' \mu / (1 + \varepsilon' + 2\mu - k)
 \end{aligned}$$

This value of ρ satisfies the eqn (8)

$$\therefore x = -\mu + \varepsilon' \mu / (1 + \varepsilon' + 2\mu - k).$$

Let L denote the equilibrium point then

$$L = L [-\mu + \varepsilon' \mu / (1 + \varepsilon' + 2\mu - k), 0, 0]$$

When no perturbations act then $\varepsilon, \varepsilon' = 0$ and $L = L (-\mu, 0, 0)$, which agrees with the Robe's result.

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Linear stability and first order normalization in planar restricted three body problem when more massive and infinitesimal bodies are oblate spheroid

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Abstract

The linear stability and first order normalization in planar restricted three body problem has been studied when more massive and infinitesimal bodies are oblate spheroid under the condition that distances from center of mass of finite bodies to infinitesimal body are same

(Keywords restricted problem of three bodies/massive body/infinitesimal body/oblate spheroid/normalization/equatorial moment of inertia/polar moment of inertia/Moser's theorem)

Introduction

Let us consider M_1 , M_2 and M are three bodies with masses $m_1 \geq m_2 \gg m$ in which M_1 and M are oblate spheroid. A and C denote the equatorial and polar moments of inertia of the body M respectively where as A_1 and C_1 for M_1 . r_i ($i = 1, 2$) be distances between the centre of mass of bodies M_i and centre of mass of body M . Let (x, y) be the co-ordinates of the infinitesimal body at any instant under the barycentric system of co-ordinates. The units are chosen as follows

- (i) $m_1 + m_2 = 1$, $\mu = m_2/(m_1 + m_2)$ and $1-\mu = m_1/(m_1 + m_2)$
- (ii) Gravitational constant = 1.
- (iii) Distance between the centre of mass of primaries = 1.

Subbarao and Sharma¹ considered the problem with one of the primaries as an oblate spheroid. It is of interest to consider the oblateness of more massive primary and infinitesimal body

Equation of Motion

Similar to Kondur and Shinkarik² the equation of motion of our structure is written as :

$$\ddot{x} - 2\dot{y} = \partial\Omega/\partial y \quad (1)$$

$$\ddot{y} + 2\dot{x} = \partial\Omega/\partial x \quad (2)$$

where, $\Omega = 1/2 (x^2 + y^2) + U_1 + U_2$

$$U_1 = m_1 \left\{ 1/r_1 + (A\sigma)/(2r_1^3) + (A_1\sigma_1)/(2r_1) \right\}$$

$$U_2 = m_2 \left\{ 1/r_2 + (A\sigma)/(2r_2^3) + (A_2\sigma_2)/(2r_2) \right\}$$

$$\sigma = \{(C-A)/A\} \quad (-1 \leq \sigma \leq 1)$$

$$\sigma_1 = \{(C_1-A_1)/A_1\} \quad (-1 \leq \sigma_1 \leq 1)$$

$$r_1^2 = (x - x_1)^2 + y^2, r_2^2 = (x - x_2)^2 + y^2 \quad (3)$$

$(x_1, 0)$ and $(x_2, 0)$ are co-ordinates of the primaries corresponding to barycentre as origin. We have $x_1 = -\mu$ and $x_2 = 1 - \mu$

$$\begin{aligned} \therefore \Omega = & (1/2)(x^2 + y^2) + (1 - \mu)/r_1 + (\mu)/(r_2) + \{(1 - \mu)A\sigma\}/r_1^3 \\ & + (\mu A\sigma)/(r_2^3) + \{(1 - \mu)(A_1\sigma_1)\}/(2r_1^3) \end{aligned} \quad (4)$$

$$\text{and } r_1^2 = (x + \mu)^2 + y^2 \quad (5)$$

$$r_2^2 = (x - 1 + \mu)^2 + y^2 \quad (6)$$

Existence of Equilibrium Point

For equilibrium position, $\partial\Omega/\partial x = 0, \partial\Omega/\partial y = 0$

$$\text{i.e. } x - \left\{ (1-\mu)(x+\mu) \right\}/r_1^3 - \left\{ \mu(x-1+\mu) \right\}/r_2^3 - (3A\sigma/2) \left[\left\{ (1-\mu)(x+\mu) \right\}/r_1^5 - \left\{ \mu(x-1+\mu) \right\}/r_2^5 \right] - (3A_1\sigma_1/2) \left\{ (1-\mu)(x+\mu) \right\}/r_1^5 = 0 \quad (7)$$

$$\text{and } y \left[1 - \left\{ (1-\mu)/r_1^3 \right\} - \left(\mu/r_2^3 \right) - (3A\sigma/2) \left\{ (1-\mu)/r_1^5 \right\} + \left(\mu/r_2^5 \right) \right. \\ \left. - (3A_1\sigma_1(1-\mu)/(2r_1^5)) \right] = 0 \quad (8)$$

For triangular libration point $x \neq 0$ and $y \neq 0$

\therefore from (8), we get.

$$\left[1 - \left\{ (1-\mu)/r_1^3 \right\} - \left(\mu/r_2^3 \right) - (3A\sigma/2) \left\{ (1-\mu)/r_1^5 \right\} + \left(\mu/r_2^5 \right) - (3A_1\sigma_1(1-\mu)/(2r_1^5)) \right] = 0 \quad (9)$$

$$\text{Multiplying eqn. (9) by } x \text{ and then subtracting from (7) and then putting, } r_1=r_2=r, \\ \text{we have } r^5 - r^2 - (3A\sigma/2) - \{A_1\sigma_1/(1-\mu)/2\} = 0 \quad (10)$$

Now we calculate the nature of r with the help of Descart's rule of sign. For the real libration point, r should be real and positive.

The changes of sign of the equation depends on the sign of σ and σ_1 .

Case 1 : When σ and σ_1 both are positive. The sign of the above equation can be written as $+-+-$.

Here we get only one change of sign. Hence we get at most one positive real value of r . Again the equation is of odd degree. So only one +ve value of r exists.

Case II : When σ is +ve and σ_1 is negative the sign of equation can be written as $+ - - +$.

Here we get two changes of sign.

∴ We get at most two +ve real value of r .

Case III : When σ is -ve and σ_1 is +ve. The change of sign is written as + - + -.

Here we get three changes of sign. We get at most three +ve real values of r

Case IV : When σ and σ_1 both are negative. The change of sign is as follow + - + +.

We get two changes of sign. Hence we get at most two +ve real values of r .

We frame a table given below :

Case No	Sign of σ	Sign of σ_1	Number of changes of sign in the equation	At most number of +ve value of r
1	+	+	1	1
2	+	-	2	2
3	-	+	3	3
4	-	-	2	2

Now we have $r_1^2 = r_2^2$

$$x = (1/2) - \mu \text{ and } y^2 = r^2 - (1/4) \text{ [From (5) and (6)]}$$

$$\therefore y = \pm \sqrt{(r^2 - 1/4)}$$

Hence triangular liberation points are $L_4 = L_4 [(1/2) - \mu, \sqrt{(r^2 - 1/4)}]$

By case 1, number of $L_4 = 1$; by case 2, number of $L_4 = 2$.

By case 3, number of $L_4 = 3$; by case 2, number of $L_4 = 2$.

$$\text{And } L_5 = L_5 [(1/2) - \mu, -\sqrt{(r^2 - 1/4)}]$$

By case 1, number of $L_5 = 1$; by case 2, number of $L_5 = 2$.

By case 3, number of $L_5 = 3$; by case 2, number of $L_5 = 2$.

Putting $r = 1$, libration points become the libration point of classical case.

Linear Stability

Since equilibrium exists at L_4 and L_5 with co-ordinates

$[(1/2) - \mu, \sqrt{r^2 - 1/4}]$ and $[(1/2) - \mu, -\sqrt{r^2 - 1/4}]$ respectively.

Firstly, we calculate the stability for L_4 with the help of Shrivastava and Garain⁴ as follows

$$\Omega_{xx}^0 = 3/(4r^5) [1 + 5A\sigma/(2r^2) + \{A_1\sigma_1(1-\mu)/(2r^2)\}] \quad (11)$$

$$\Omega_{xy}^0 = \Omega_{yx}^0 = \{+\sqrt{(r^2 - 1/4)/(2r^5)}\} [3(1-\sigma)\mu + \{15/(2r^5)\} A\sigma(1-2\mu) - A_1\sigma_1(1-\mu)] \quad (12)$$

$$\Omega_{yy}^0 = (1/r^5) [(r^2 - 1/4) \{3 + 15A\sigma/(2r^2) + 15A_1\sigma_1(1-\mu)/(2r^2)\}]$$

(0) indicates that (x, y) are replaced by (x_0, y_0) after proper differentiation when (x_0, y_0) is the equilibrium point.

∴ Characteristic equation regarding L_4 can be written as

$$\begin{aligned} & \lambda^4 + \lambda^2 [4 - (3/r^5) \{1 + 5A\sigma/(2r^2) + 5A_1\sigma_1(1-\mu)/(2r^2)\} - \\ & \{ (r^2 - 1/4)/r^5 \} \{3 + 15A\sigma/(2r^2) + 15A_1\sigma_1(1-\mu)/(2r^2)\}] + 3/(4r^{10}) \\ & \{1 + 5A\sigma/(2r^2) + 15A_1\sigma_1(1-\mu)/(2r^2)\} [(r^2 - 1/4)/r^5] \{3 + 15A\sigma/(2r^2) \\ & + 15A_1\sigma_1(1-\mu)/(2r^2)\} - [\{\sqrt{(r^2 - 1/4)/(2r^5)}\} 3(1-2\mu) \\ & + \{15A\sigma(1-2\mu)/(2r^2) - 15A_1\sigma_1(1-\mu)/(2r^2)\}] = 0 \end{aligned} \quad (14)$$

Eqn. (14) is a biquadratic equation in λ . Hence it is a quadratic equation in λ^2 .

$$\therefore \lambda^2 = \{-Q \pm \sqrt{Q^2 - 4PR}\} / (2P)$$

where, $P = 1$,

$$Q = 4 - \{3/(5r^5) [\{1 + 5A\sigma/(2r^2) + A_1\sigma_1(1-\mu)/(2r^2)\} \{(r^2-1/4)/r^5\}$$

$$\{3 + 15A\sigma/(2r^2) + 15A_1\sigma_1(1-\mu)/(2r^2)\}]\}$$

$$\text{and } R = 3/(4r^{10}) \{1 + 5A\sigma/(2r^2) + 5A_1\sigma_1(1-\mu)/(2r^2)\} \{3 + 15A\sigma/(2r^2)$$

$$+ 15A_1\sigma_1(1-\mu)/(2r^2)\} (r^2-1/4) - [\sqrt{(r^2-1/4)/2r^5} \{3(1-2\mu)$$

$$+ 15A\sigma/(1-2\mu)/(2r^2) - \{15A_1\sigma_1(1-\mu)/(2r^2)\}]\}$$

For critical mass μ_c , $Q^2 - 4PR = 0$ and the characteristic roots are of conjugate pair. Hence L_4 is stable in this case otherwise L_4 is unstable. In the similar way the condition for stability of $L_5(1/2-\mu, -\sqrt{(r^2-1/4)})$ can be obtained.

First Order Normalization

The Lagrangian function of the problem is written as

$$L = (1/2) \left(\dot{x}^2 + \dot{y}^2 \right) + (xy + y\dot{x}) + (1/2) \left(x^2 + y^2 \right) + (1-\mu)/r_1 + \mu/r_2 + \\ \{(A\sigma)/2\} \left\{ (1-\mu)/r_1^3 + \mu/r_2^3 \right\} + \{(A_1\sigma_1)/2\} \left\{ (1-\mu)/r_1^3 \right\} \quad (15)$$

where $r_1^2 = (x + \mu)^2 + y^2$, $r_2^2 = (x - 1 - \mu)^2 + y^2$ and triangular liberation point L_4 is $[(1/2) - \mu, \sqrt{(r^2 - 1/4)}]$ in which r is obtained from the eqn. (10).

L_4 can be written as $(r/2, r'/2)$. Now we shift the origin to L_4 . Then $x \rightarrow x + (Y/2)$, $y \rightarrow y + (Y'/2)$

∴ Eqn (15) reduces to

$$\begin{aligned}
 L = & (1/2) (\dot{x}^2 + \dot{y}^2) + [\{x + (Y/2)\} \dot{y} - \{y + (Y/2)\} \dot{x}] + (1/2) [\{x + (Y/2)\}^2 \\
 & + \{y + (Y/2)\}^2] + (1-\mu)/r_1 + \mu/r_2 + \{(A\sigma)/2\} \{(1-\mu)/r_1^3 + \mu/r_2^3\} \\
 & + \{(A_1\sigma_1)/2\} \{(1-\mu)/r_1^3\}
 \end{aligned} \quad (16)$$

where

$$r_1^{-1} = [\{x + (1/2)\}^2 + \{y + (Y/2)\}^2]^{-1/2} = f(x, y) \quad (17)$$

$$r_2^{-1} = [\{x - (1/2)\}^2 + \{y + (Y/2)\}^2]^{-1/2} = g(x, y) \quad (18)$$

$$r_1^{-3} = [\{x + (1/2)\}^2 + \{y + (Y/2)\}^2]^{-3/2} = f_1(x, y) \quad (19)$$

$$r_2^{-3} = [\{x - (1/2)\}^2 + \{y + (Y/2)\}^2]^{-3/2} = g_1(x, y) \quad (20)$$

Expanding these in power series and substituting them in eqn. (16) and arranging the terms in ascending power of x, y ; L can be written as $L = L_0 + L_1 + L_2 + L_3 + L_4 + \dots$ and Lagranges equation of motions are

$$\begin{aligned}
 \text{i.e. } \ddot{x} - 2\dot{y} = & \{1 - (1/r^3) - 3A\sigma/(2r^5) - 3A_1\sigma_1(1-\mu)/(2r^5) + 3/(4r^5) + 15A\sigma/(8r^7) \\
 & + 15A_1\sigma_1(1-\mu)/(8r^7)\} x + \{3\sqrt{(4r^2-1)/(4r^5)} + 15A\sigma\sqrt{(4r^2-1)/(8r^7)} \\
 & - 3\mu\sqrt{(4r^2-1)/(2r^5)} - 15A\sigma\mu\sqrt{(4r^2-1)/(4r^7)} \\
 & + 15A_1\sigma_1(1-\mu)\sqrt{(4r^2-1)/(8r^7)}\} y
 \end{aligned} \quad (21)$$

and

$$\ddot{y} + 2\dot{x} = \{(4r^2-1)/(4r^5) + 3 - (1/r^3) - 15A\sqrt{(4r^2-1)/(8r^7)} - 3\mu\sqrt{(4r^2-1)/(2r^7)}$$

$$\begin{aligned}
& -15A\sigma\mu\sqrt{(4r^2-1)/(4r^7)} + 15A_1\sigma_1(1-\mu)\sqrt{(4r^2-1)/(8r^7)}\}x + \{1-(1/r^3) \\
& - 3A\sigma/(2r^5) - 3A_1\sigma_1(1-\mu)/(2r^5) + 3(4r^2-1)/(4r^5) \\
& + 15A\sigma(4r^2-1)/(8r^7) + 15A_1\sigma_1(1-\mu)(4r^2-1)/(8r^7)\}y
\end{aligned} \tag{22}$$

The characteristic equation is given by

$$\begin{aligned}
& \lambda^4 + \lambda^2 \{4-(3/r^3) - 15A\sigma/(2r^5) + 15A_1\sigma_1(1-\mu)/(2r^5)\} \\
& + \{3/(4r^{10})\} \{1+5A\sigma/(2r^2) + 5A_1\sigma_1(1-\mu)/(2r^2)\} [\{3+15A\sigma/(2r^2) \\
& + 15A_1\sigma_1(1-\mu)/(2r^2)\} (4r^2-1)/4\} \} - [\{\sqrt{(4r^2-1)/(4r^5)}\} \{3(1-2\mu) \\
& + 15(1-2\mu) A\sigma/(2r^2) - 15A_1\sigma_1(1-\mu)/(2r^2)\}]^2 = 0.
\end{aligned} \tag{23}$$

Let $\lambda = iw_1, \lambda_2 = iw_2, \lambda_3 = -iw_1, \lambda_4 = -iw_2$,

Then

$$\begin{aligned}
w_1^2 + w_2^2 &= \{4-(3/r^3)\} - 15A\sigma/(2r^5) - 15A_1\sigma_1(1-\mu)/(2r^5) \\
w_1^2 \cdot w_2^2 &= \{3/(4r^{10})\} \{1+5A\sigma/(2r^2) + 5A_1\sigma_1(1-\mu)/(2r^2)\} [3+15A\sigma/(2r^2) \\
& + 15A_1\sigma_1(1-\mu)/(2r^2)] \{(4r^2-1)/4\} - [\{\sqrt{(4r^2-1)/(4r^5)}\} \{3(1-2\mu) \\
& + 15(1-2\mu) A\sigma/(2r^2) - 15A_1\sigma_1(1-\mu)/(2r^2)\}]^2
\end{aligned}$$

By applying Moser's theorem³ and following Garain and Shrivastava⁵ we have

$$\begin{aligned}
\mu_1 &= 1/2[1-\{1+(5/3)(r^8-r^2) + (25/9)(r^{13}-2r^{10}+r^7) - (64/225)r^{10}/(4r^2-1) \\
&\quad (4-3/r^3-5r^5+5r^2)^2\}^{1/2}] / [1+5A\sigma/(2r^2) - (5/4)A_1\sigma_1/r^2] \\
\mu_2 &= 1/2[1-\{1+(5/3)(r^8-r^2) + (25/9)(r^{13}-2r^{10}+r^7) - (16/100)r^{10}
\end{aligned}$$

$$(4-3/r^3 - 5r^5 + 5r^2) / (4r^2-1)^{1/2}]/[1+5 A\sigma/2r^2) - (5/4) A_1\sigma_1/r^2]$$

The Hamiltonian corresponding to Lagrange's function is given by

$$H = -L + P_x x + P_y Y.$$

$$= 1/2(P_x^2 + P_y^2) + (yP_x - xP_y) - (1-\mu)/r_1 - \mu/r_1 - (A\sigma/2) \left\{ \left((1-\mu)/r_1^3 + \mu r_2^3 \right) \right. \\ \left. \left\{ (A_1\sigma_1/2) (1-\mu) / r_1^3 \right\} \right.$$

Let us transform $x \rightarrow x + \gamma/2$, $y \rightarrow y + \gamma/2$, $P_x \rightarrow P_x - \gamma/2$, $P_y \rightarrow P_y + \gamma/2$,

We get Hamiltonian

$$H = H_0 + H_1 H_2 + H_3 + H_4 + \dots$$

where, $H_0 = -(\gamma^2/8) - (\gamma^2/8) - (1/r) - (A\sigma/2r^2) - A_1\sigma_1 (1-\mu)/(2r^3)$

$$H_1 = x \left\{ -(\gamma/2) + 1/(2r^3) - \mu/r^3 + 3A\sigma/(4r^5) - \frac{3A\sigma\mu}{2r^5} \right. \\ \left. - 3A_1\sigma_1 (1-\mu)/(4r^5) + \gamma y \left\{ -1/2 + 1/(2r^3) + 3A\sigma/(4r^5) \right. \right. \\ \left. \left. - 3A_1\sigma_1 (1-\mu)/(2r^5) \right\} \right\} \\ H_2 = 1/2(P_x^2 + P_y^2) + (yP_x - xP_y) + x^2 \left\{ 1/(2r^3) - 3/(8r^5) + (3/4) A\sigma/r^5 \right. \\ \left. - (15/16) A\sigma/r^7 + (3/4) A_1\sigma_1 (1-\mu)/(4r^5) - (15/16) A_1\sigma_1 (1-\mu)/r^7 \right\} \\ + y^2 \left\{ 1/(2r^3) - (3/8) (4r^2 - 1)/r^5 + (3/4) A\sigma/r^5 \right. \\ \left. - (15/16) A\sigma (4r^2 - 1)/r^7 + (3/4) A_1\sigma_1 (1-\mu)/(4r^5) \right\}$$

$$\begin{aligned}
& - (15/16) A_1 \sigma_1 (4r^2 - 1) (1 - \mu)/r^7 \} + \gamma^1 xy \{ (-3/4)/r^5 + (3/2)\mu/r^5 \\
& - (15/8) A\sigma/r^7 + (15/4) A\sigma/r^7 - (15/8) A_1 \sigma_1 (1 - \mu)/r^7 \}
\end{aligned}$$

Now we find the canonical transformation from phase space (x, y, p_x, p_y) in to phase space product of angle co-ordinates (ϕ_1, ϕ_2) and action moment (I_1, I_2) and first order in $I_1^{1/2}, I_2^{1/2}$, so that second order part of the Hamiltonian is normalized. For this we follow the method adopted by Whittaker⁶

We consider $-\lambda P_x = \partial H_2/\partial x, -\lambda P_y = \partial H_2/\partial y, \lambda x = \partial H_2/\partial P_x, \lambda y = \partial H_2/\partial P_y$, which gives the following results .

$$\begin{aligned}
& 2bx + dy + \lambda P_x - ap_y = 0 \\
& dx + 2cy + ap_x + \lambda P_y = 0 \\
& \lambda x - ay - P_x = 0 \\
& ax + \lambda y - P_y = 0
\end{aligned} \tag{24}$$

where, $a = 1$

$$\begin{aligned}
b &= (1/2)/r^3 - (3/8)/r^5 + (3/4)A\sigma/r^5 - (15/16) A\sigma/r^7 \\
&+ (3/4) A_1 \sigma_1 (1 - \mu)/r^5 - (15/16) A_1 \sigma_1 (1 - \mu)/r^7 \\
c &= (1/2)/r^3 - (3/8) (4r^2 - 1)/r^5 + (3/4)A\sigma/r^5 - (15/16) A\sigma(4r^2 - 1)/r^7 \\
&+ (3/4) A_1 \sigma_1 (1 - \mu)/r^5 - (15/16) A_1 \sigma_1 (1 - \mu)(4r^2 - 1)/r^7 \\
d &= \gamma^1 (-3/4)/r^5 + (3/2)\mu/r^5 - (15/8) A\sigma/r^7 + (15/4) A\sigma\mu/r^7 \\
&- (15/8) A_1 \sigma_1 (1 - \mu)/r^7
\end{aligned}$$

solving eqn. (24), we get

$$x/(-d + 2a\lambda) = y/(2b + \lambda^2 - a^2) = P_x/(a\lambda^2 - \lambda d - 2ab + a^3)$$

$$= P_y / (\lambda^3 + a2\lambda + 2b\lambda - ad) = K.$$

we have four values of λ and consequently four values of K . We consider the transformation (x, y, P_x, P_y) to (q_1, q_2, p_1, p_2) similar to Garain and Shrivastava⁵ and get

$$H_2 = \sum_{j=1}^2 \lambda_j q_j p_j = \sum_{j=1}^2 i w_j q_j p_j, \text{ where } i = \sqrt{(-1)}$$

Again we transform (q_1, q_2, p_1, p_2) to (Q_1, Q_2, P_1, P_2) similar to Garain and Shrivastava⁵ and get

$$Q_j = (2I_j/W_j)^{1/2} \sin \Phi_j, \quad P_j = (2I_j/W_j)^{1/2} \cos \Phi_j, \quad (j = 1, 2).$$

Then the canonical transformation of phase space (X, Y, P_x, P_y) in to phase space product of angle co-ordinates (Φ_1, Φ_2) and action momenta (I_1, I_2) is given by

$$\begin{pmatrix} X \\ Y \\ P_x \\ P_y \end{pmatrix} = A \begin{pmatrix} Q_1 \\ Q_2 \\ P_x \\ P_y \end{pmatrix}$$

where $A = J_1 J_2 = (a_{rs})$ ($r, s = 1, 2, 3, 4$)

$$a_{11} = x_1 - x_3 i w_1 / 2 = k_1 (2a\lambda_1 - d) - k_3 i w_1 (2a\lambda_3 - d) / 2$$

$$a_{12} = x_2 - x_4 i w_2 / 2 = k_2 (2a\lambda_2 - d) - k_4 i w_2 (2a\lambda_4 - d) / 2$$

k_j ($j = 1, 2, 3, 4$) can be made to satisfy the two condition $a_{11} = a_{12} = 0$, which gives

$$k_1 / \{(w_1/2)(2aw_1 - id)\} = k_3 / \{2aiw_1 - c'\} = h_1$$

$$k_2 / \{(w_2/2)(2aw_2 - id)\} = k_4 / \{-(2aiw_2 - d)\} = h_2$$

other values of a_{rs} can be obtained

$$a_{rs} = a_{rs} (k, w_1, w_2, \mu, r, \sigma, \sigma_1, m_j, n_j, P_j)$$

$$\text{where } m_j = 4w_j^2 + 4 - 3/r^3 - (15/2)A\sigma/r^5 - (15/2)A_1\sigma_1(1-\mu)/r^5$$

$$l_j^2 = 4w_j^2 + 12 - 3/r^3 - 6A\sigma/r^5 - (9/2)A_1\sigma_1(1-\mu)/r^5$$

$$P_j = 4w_j^2 + 3/r^3 - (9/2)A\sigma/r^5 - (15/2)A_1\sigma_1(1-\mu)/r^5, (j = 1, 2)$$

Thus H is normalized to

$$H = W_1 I_1 - W_2 I_2$$

Taking $H = H_0 + H_1 + H_2$, the equation of motion can be written as

$$dI_j/dt = -\partial H / \partial \Phi_j, \quad d\Phi_j/dt = \partial H / \partial I_j, \quad (j = 1, 2)$$

$$dI_j/dt = 0, \quad d\Phi_1/dt = w_1, \quad d\Phi_2/dt = -w_2.$$

The general solution is

$$I_j = \text{constant. } (j = 1, 2)$$

$$\Phi_j = (-1)^{j+1} w_j t + \text{constant.}$$

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Integrals involving product of $H[x,y]$ and the generalized polynomials $S_{n_1, \dots, n_r}^{m_1, \dots, m_r}[x]$

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Abstract

The aim of this paper is to evaluate two integrals involving product of the H -function of two variables $H[x, y]$ and the generalized polynomials $S_{n_1, \dots, n_r}^{m_1, \dots, m_r}[x]$. The values of the two integral are obtained in terms of $\psi(z)$, the logarithmic derivative of $\Gamma(z)$.

(Keywords : H -function of two variables/generalized polynomials/logarithmic derivative).

Introduction

(a) The general class of polynomials $S_{n_1, \dots, n_r}^{m_1, \dots, m_r}[x]$ is defined and represented¹ as follows:

$$S_{n_1, \dots, n_r}^{m_1, \dots, m_r}[x] = \sum_{k_1=0}^{\lfloor n_1/m_1 \rfloor} \dots \sum_{k_r=0}^{\lfloor n_r/m_r \rfloor} \prod_{i=1}^r \frac{(-n_i)_{m_i k_i}}{k_i!} A_{n_i, k_i} x^{k_i} \quad (1)$$

where $n_1, \dots, n_r = 0, 1, 2, \dots$; m_1, \dots, m_r are arbitrary positive integers, the coefficients A_{n_i, k_i} ($n_i, k_i \geq 0$) are arbitrary constants, real or complex.

(b) The H -function of two variables is defined and represented² as follows:

$$\begin{aligned}
H[x, y] &= H_{p_1, q_1, p_2, q_2, p_3, q_3}^{0, n_1, m_2, n_2, m_3, n_3} \left[\begin{array}{c|c} x & (a_j; \alpha_j, A_j)_{1, p_1} : (c_j, \gamma_j)_{1, p_2} : (e_j, E_j)_{1, p_3} \\ \hline y & (b_j; \beta_j, B_j)_{1, q_1} : (d_j, \delta_j)_{1, q_2} : (f_j, F_j)_{1, q_3} \end{array} \right] \\
&= -\frac{1}{4\pi^2} \int_{L_1} \int_{L_2} \phi(\xi, \eta) \theta_1(\xi) \theta_2(\eta) x^\xi y^\eta d\xi d\eta \quad (2)
\end{aligned}$$

where

$$\phi(\xi, \eta) = \frac{\prod_{j=1}^{n_1} \Gamma(1 - a_j + \alpha_j \xi + A_j \eta)}{\prod_{j=n_1+1}^{p_1} \Gamma(a_j - \alpha_j \xi - A_j \eta) \prod_{j=1}^{q_1} \Gamma(1 - b_j + \beta_j \xi + B_j \eta)} \quad (3)$$

$$\theta_1(\xi) = \frac{\prod_{j=1}^{n_2} \Gamma(1 - c_j + \gamma_j \xi) \prod_{j=1}^{m_2} \Gamma(d_j - \delta_j \xi)}{\prod_{j=n_2+1}^{p_2} \Gamma(c_j - \gamma_j \xi) \prod_{j=m_2+1}^{q_2} \Gamma(1 - d_j + \delta_j \xi)} \quad (4)$$

and $\theta_2(\eta)$ is defined similarly.

The contour L_1 is in the ξ -plane and runs from $-i\infty$ to $i\infty$, with loops, if necessary, to ensure that the poles of $\Gamma(d_j - \delta_j \xi)$ ($j = 1, \dots, m_2$) lie to the right and the poles of $\Gamma(1 - c_j + \gamma_j \xi)$ ($j = 1, \dots, n_2$), $\Gamma(1 - a_j + \alpha_j \xi + A_j \eta)$ ($j = 1, \dots, n_1$) to the left of the contour. L_2 is similarly defined.

It is assumed that the existence and convergence conditions are satisfied for the various H -functions of 2-variables occurring here.

By summing up the residues at the simple poles of the integral of (2), we have the following expansion² for $H[x, y]$:

$$H_{p_1, q_1, p_2, q_2, p_3, q_3}^{0, m_1-1, m_2, 1, m_3} [x, y] = \sum_{h=0}^{\infty} \sum_{\ell=0}^{\infty} \left\{ \frac{(-1)^{h+\ell}}{h! \ell!} f(\zeta_1, \zeta_2) \frac{x^{\zeta_1} y^{\zeta_2}}{\delta_1 F_1} \right\} \quad (5)$$

where $\zeta_1 = \frac{d_1 + h}{\delta_1}$, $\zeta_2 = \frac{f_1 + \ell}{F_1}$, $h, \ell = 0, 1, 2, \dots$ (6)

and

$$f(\zeta_1, \zeta_2) = \phi(\zeta_1, \zeta_2) \theta_1^*(\zeta_1) \theta_2^*(\zeta_2) \quad (7)$$

where $\phi(\zeta_1, \zeta_2)$ is given by (3),

$$\theta_1^*(\zeta_1) = \frac{\prod_{j=1}^{m_2} \Gamma(1 - c_j + \gamma_j \zeta_1)}{\prod_{j=m_2+1}^{p_2} \Gamma(c_j - \gamma_j \zeta_1) \prod_{j=1}^{q_2} \Gamma(1 - d_j + \delta_j \zeta_1)} \quad (8)$$

and $\theta_2^*(\zeta_2)$ is defined similarly.

Main Integrals

Let $\psi(z)$ denote the logarithmic derivative of gamma function $\Gamma(z)$ i.e.
 $\psi(z) = \frac{\Gamma'(z)}{\Gamma(z)}.$

Also, let $E(x) = \{2 + \lambda_1(1-x) + \lambda_2(1+x)\}$ (9)

and

$$G(x) = \frac{(1-x)^{a-1} (1+x)^{b-1}}{\{E(x)\}^{a+b}} S_{m_1, \dots, m_r}^{m_1, \dots, m_r} \left[c \prod_{i=1}^r \frac{(1-x)^{s_i} (1+x)^{t_i}}{\{E(x)\}^{s_i+t_i}} \right]$$

$$H \left[\begin{array}{c} \frac{y(1-x)^{\mu_1} (1+x)^{\nu_1}}{\{E(x)\}^{\mu_1+\nu_1}} \\ \frac{z(1-x)^{\mu_2} (1+x)^{\nu_2}}{\{E(x)\}^{\mu_2+\nu_2}} \end{array} \right] \quad (10)$$

We have

$$\begin{aligned} \int_{-1}^1 G(x) \log \left[\frac{(1-x)}{E(x)} \right] dx &= \frac{1}{2} \sum_{k_1=0}^{[n_1/m_1]} \dots \sum_{k_r=0}^{[n_r/m_r]} \sum_{h=0}^{\infty} \sum_{\ell=0}^{\infty} \\ &\left[\prod_{i=1}^r \frac{(-n_i)_{m_i k_i}}{k_i!} A_{n_i k_i} c^{k_i} \frac{(-1)^{h+\ell}}{h! \ell!} (1+\lambda_1)^{-a-s_i k_i - \mu_1 \zeta_1 - \mu_2 \zeta_2} (1+\lambda_2)^{-b-t_i k_i - \nu_1 \zeta_1 - \nu_2 \zeta_2} \right. \\ &\left. \frac{F(\zeta_1, \zeta_2)}{\delta_1 F_1} \{-\log(1+\lambda_1) + \psi(a+s_i k_i + \mu_1 \zeta_1 + \mu_2 \zeta_2) - \psi(a+b+k_i(s_i+t_i) \right. \\ &\left. + (\mu_1 + \nu_1) \zeta_1 + (\mu_2 + \nu_2) \zeta_2) \} y^{\zeta_1} z^{\zeta_2} \right] \quad (11) \end{aligned}$$

and

$$\begin{aligned} \int_{-1}^1 G(x) \log \left[\frac{(1+x)}{E(x)} \right] dx &= \frac{1}{2} \sum_{k_1=0}^{[n_1/m_1]} \dots \sum_{k_r=0}^{[n_r/m_r]} \sum_{h=0}^{\infty} \sum_{\ell=0}^{\infty} \\ &\left[\prod_{i=1}^r \frac{(-n_i)_{m_i k_i}}{k_i!} A_{n_i k_i} c^{k_i} \frac{(-1)^{h+\ell}}{h! \ell!} (1+\lambda_1)^{-a-s_i k_i - \mu_1 \zeta_1 - \mu_2 \zeta_2} (1+\lambda_2)^{-b-t_i k_i - \nu_1 \zeta_1 - \nu_2 \zeta_2} \right. \\ &\left. \frac{F(\zeta_1, \zeta_2)}{\delta_1 F_1} \{-\log(1+\lambda_2) + \psi(b+t_i k_i + \nu_1 \zeta_1 + \nu_2 \zeta_2) - \psi(a+b+k_i(t_i+s_i) \right. \\ &\left. + (\mu_1 + \nu_1) \zeta_1 + (\mu_2 + \nu_2) \zeta_2) \} y^{\zeta_1} z^{\zeta_2} \right]. \quad (12) \end{aligned}$$

where

$$F(\zeta_1, \zeta_2) = f(\zeta_1, \zeta_2) B(a+s_i k_i + \mu_1 \zeta_1 + \mu_2 \zeta_2, b+t_i k_i + v_1 \zeta_1 + v_2 \zeta_2), \quad (13)$$

$i = 1, \dots, r$; ζ_1, ζ_2 and $f(\zeta_1, \zeta_2)$ are given by (6) and (7).

(11) and (12) are valid for

$$(i) \quad |\arg y| < \frac{U\pi}{2}, \quad |\arg z| < \frac{V\pi}{2}, \quad (14)$$

where

$$U = - \sum_{j=N_1+1}^R \alpha_j - \sum_{j=1}^{Q_1} \beta_j - \sum_{j=1}^{Q_2} \delta_j + \sum_{j=1}^{N_2} \gamma_j - \sum_{j=N_2+1}^{P_2} \gamma_j > 0,$$

$$V = - \sum_{j=N_1+1}^R A_j - \sum_{j=1}^{Q_1} B_j - \sum_{j=1}^{Q_3} F_j + \sum_{j=1}^{N_3} E_j - \sum_{j=N_3+1}^{P_3} E_j > 0.$$

(ii) $a, b, \mu_1, \mu_2, v_1, v_2$ are all positive, and

$$\begin{aligned} Re(a) + \mu_1 [Re(d_1/\delta_1)] + \mu_2 [Re(f_1/F_1)] &> 0, \\ Re(b) + v_1 [Re(d_1/\delta_1)] + v_2 [Re(f_1/F_1)] &> 0. \end{aligned} \quad (15)$$

To establish the results in (11) and (12), we require the following integral :

$$I = \int_{-1}^1 \frac{(1-x)^{a-1} (1+x)^{b-1}}{\{E(x)\}^{a+b}} S_{m_1, \dots, m_r}^{m_1, \dots, m_r} \left[c \prod_{i=1}^r \frac{(1-x)^{s_i} (1+x)^{t_i}}{\{E(x)\}^{s_i+t_i}} \right]$$

$$\begin{aligned}
& H_{\beta_1, \beta_2, \beta_3, \beta_4, \beta_5, \beta_6}^{0, N_1, 1, N_2, 1, N_3} \left[\begin{array}{c} y(1-x)^{\mu_1} (1+x)^{\nu_1} \\ \{E(x)\}^{\mu_1+\nu_1} \\ z(1-x)^{\mu_2} (1+x)^{\nu_2} \\ \{E(x)\}^{\mu_2+\nu_2} \end{array} \right] dx \\
& = \frac{1}{2} \sum_{k_1=0}^{[n_1/m_1]} \dots \sum_{k_r=0}^{[n_r/m_r]} \left\{ \prod_{i=1}^r \frac{(-n_i)_{m_i k_i}}{k_i!} A_{n_i, k_i} c^{k_i} (1+\lambda_1)^{-a-s_i k_i} (1+\lambda_2)^{-b-t_i k_i} \right. \\
& \quad \left. H_{\beta_1+2, \beta_2+1, \beta_3, \beta_4, \beta_5, \beta_6}^{0, N_1+2, 1, N_2, 1, N_3} \left[\begin{array}{c} y(1+\lambda_1)^{-\mu_1} (1+\lambda_2)^{-\nu_1} \\ z(1+\lambda_1)^{-\mu_2} (1+\lambda_2)^{-\nu_2} \end{array} \right| \begin{array}{c} P \cdot (c_j, \gamma_j)_{1, P_1}, (e_j, \beta_j)_{1, P_2} \\ Q \cdot (d_j, \delta_j)_{1, Q_1}, (f_j, F_j)_{1, Q_2} \end{array} \right] \quad (16) \\
& = \frac{1}{2} \sum_{k_1=0}^{[n_1/m_1]} \dots \sum_{k_r=0}^{[n_r/m_r]} \sum_{h=0}^{\infty} \sum_{\ell=0}^{\infty} \left\{ \prod_{i=1}^r \frac{(-n_i)_{m_i k_i}}{k_i!} A_{n_i, k_i} c^{k_i} \frac{(-1)^{h+\ell}}{h! \ell!} \right. \\
& \quad \left. (1+\lambda_1)^{-a-s_i k_i - \mu_1 \zeta_1 - \mu_2 \zeta_2} (1+\lambda_2)^{-b-t_i k_i - \nu_1 \zeta_1 - \nu_2 \zeta_2} \frac{F(\zeta_1, \zeta_2) y^{\zeta_1} z^{\zeta_2}}{\delta_1 F_1} \right\}, \quad (17)
\end{aligned}$$

with ζ_1, ζ_2 given by (6) and $F(\zeta_1, \zeta_2)$ given by (13) and

$$P = (1-a-s_i k_i; \mu_1, \mu_2), (1-b-t_i k_i; \nu_1, \nu_2), (a_j; \alpha_j, A_j)_{1, P_1}$$

$$Q = (b_j; \beta_j, B_j)_{1, Q_1}, (1-a-b-k_i(s_i + t_i); \mu_1 + \nu_1, \mu_2 + \nu_2),$$

where $i = 1, \dots, r$.

To evaluate I , we substitute for $S_{n_1, \dots, n_r}^{m_1, \dots, m_r}[x]$ from eqn. (1), change the order of integration and summation, put the value of $H[x, y]$ from (2), change the order of integration and integrate the x -integral with the help of Gradshteyn and Ryzhik³

$$\begin{aligned}
 & \int_a^b \frac{(t-a)^{\alpha-1} (b-t)^{\beta-1}}{\{b-a+\lambda(t-a)+\mu(b-t)\}^{\alpha+\beta}} dt \\
 &= \frac{(1+\lambda)^{-\alpha} (1+\mu)^{-\beta}}{b-a} \frac{\Gamma(\alpha)\Gamma(\beta)}{\Gamma(\alpha+\beta)} \quad (18)
 \end{aligned}$$

$a \neq b$, $\operatorname{Re}(\alpha) > 0$, $\operatorname{Re}(\beta) > 0$, $b-a+\lambda(t-a)+\mu(b-t) \neq 0$ }, interpret the ξ , η -integral in terms of the H -function of two variables, we arrive at the right hand side of (16).

Method of Proof: The result in (11) is established by taking the partial derivative of both sides of (17) with respect to a . (12) is similarly established by taking the partial derivative of (17) with respect to b .

Special Cases

In view of the presence of a large number of parameters in (11), (12), number of special cases can be obtained. However, we give here only one special case

If, in (11), we take $\lambda_1 = \lambda_2 = 0$, it reduces to the following:

$$\begin{aligned}
 & \int_{-1}^1 (1-x)^{\alpha-1} (1+x)^{\beta-1} S_{n_1, \dots, n_r}^{m_1, \dots, m_r} \left[c \prod_{i=1}^r \frac{(1-x)^{s_i} (1+x)^{t_i}}{(2)^{s_i+t_i}} \right] \\
 & H \left[\frac{\frac{y(1-x)^{\mu_1} (1+x)^{\nu_1}}{(2)^{\mu_1+\nu_1}}}{\frac{z(1-x)^{\mu_2} (1+x)^{\nu_2}}{(2)^{\mu_2+\nu_2}}} \right] \log \left[\frac{(1-x)}{2} \right] dx \\
 & = 2^{a+b-1} \sum_{k_1=0}^{\lfloor n_1/m_1 \rfloor} \dots \sum_{k_r=0}^{\lfloor n_r/m_r \rfloor} \sum_{h=0}^{\infty} \sum_{\ell=0}^{\infty} \left[\prod_{i=1}^r \frac{(-n_i)_{m_i k_i}}{k_i!} A_{n_i, k_i} c^{k_i} \frac{(-1)^{h+\ell}}{h! \ell!} \frac{F(\zeta_1, \zeta_2)}{\delta_1 F_1} \right]
 \end{aligned}$$

$$\begin{aligned}
 & \left\{ \psi(a + s_i k_i + \mu_1 \zeta_1 + \mu_2 \zeta_2) - \psi(a + b + k_i(s_i + t_i) + (\mu_1 + \nu_1) \zeta_1 \right. \\
 & \left. + (\mu_2 + \nu_2) \zeta_2) \right\} y^{\zeta_1} z^{\zeta_2} \Big] \dots \quad (19)
 \end{aligned}$$

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Certain transformation formulae for basic hypergeometric functions of two-variable

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Abstract

Making use of a known result we establish summation formulae for basic hypergeometric functions of two variables

(Keywords : basic hypergeometric function/summation/Appel function)

Introduction

Srivastava and Jain¹ established the following identity.

$$\begin{aligned} & \sum_{l,m=0}^{\infty} \Omega_{l+m}(\lambda; q)_l (\mu; q)_m \frac{(\mu z)^l z^m}{(q; q)_l (q; q)_m} \\ & \sum_{n=0}^{\infty} \Omega_n(\lambda \mu, q)_n \frac{z^n}{(q; q)_n} \end{aligned} \tag{1}$$

where $\{\Omega_n\}_{n=0}^{\infty}$ is a bounded sequence of complex numbers and the parameters λ and μ are essentially arbitrary

Notations and Definitions

A basic hypergeometric series is given by

$${}_r\phi_s \left[\begin{matrix} a_1, a_2, \dots, a_r; q, z \\ b_1, b_2, \dots, b_s; \end{matrix} \right] \\ \sum_{n=0}^{\infty} q^{\binom{n}{2}} \frac{(a_1, a_2, \dots, a_r; q)_n}{(q, b_1, b_2, b_3, \dots, b_s, q)_n} z^n, \quad (2)$$

$$\text{where } \binom{n}{2} = \frac{n(n-1)}{2} \text{ and } (a_1, a_2, \dots, a_r, q)_n = (a_1, q)_n (a_2, q)_n \dots (a_r, q)_n \quad (3)$$

with the q -shifted factorials defined by

$$(a; q)_n = \left\{ \begin{array}{ll} 1 & \text{if } n = 0 \\ (1-a)(1-aq) \dots (1-aq^{n-1}) & \text{if } n = 1, 2, \dots \end{array} \right\}$$

$$(a; q)_{\infty} = \sum_{k=0}^{\infty} (1-aq^k) \quad (5)$$

$$(a; q)_n = \frac{(a; q)_{\infty}}{(aq^n; q)_{\infty}} \quad (6)$$

For convergence of the series (2), we need $|q| < 1$ and $|z| < \infty$, when $i = 1, 2$, or $\max(|q|, |z|) < 1$ when $i = 0$, provided that no zero appear in the denominator

A generalized basic hypergeometric series of two variables is defined as

$${}_4\phi_3 \left[\begin{matrix} (a); (b); (b'); q, x, y \\ (c); (d); (d'); \end{matrix} \right]$$

$$\sum_{m,n=0}^{\infty} q^{k m n + i \binom{m}{2} + j \binom{m}{2}} \times$$

$$\frac{\prod_{r=1}^A \pi(a_r, q)_{m+n} \prod_{r=1}^B (b_r, q)_m \prod_{r=1}^{B'} (b'_r, q)_n x^m y^n}{\prod_{r=1}^C \pi(c_r, q)_{m+n} \prod_{r=1}^D (d_r, q)_m \prod_{r=1}^{D'} (d'_r; q)_n (q, q)_m (q, q)_n} \quad (6)$$

The double series converges absolutely for all bounded values of the complex arguments x and y when $i, j, k \in N$ and $|q| < 1$ and also when $i = j = k = 0$ provided that $\max(|q|, |x|, |y|) < 1$

Appell functions of first kind is defined as :

$$\phi^{(1)}[a, b, b', c; x, y] = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{(a, q)_{m+n} (b, q)_m (b', q)_n x^m y^n}{(c; q)_{m+n} (q, q)_m (q, q)_n} \quad (7)$$

Main Results

Here we shall establish following summation formulae .

$$(a) \text{ If we choose } \Omega_n = \frac{(a, q)_n}{(a \lambda \mu z, q)_n} \quad \text{in (1),}$$

We get

$$\phi^{(1)}[a, \lambda, \mu, a \lambda z, \mu z, z] = {}_2\phi_1 \left[\begin{matrix} a, \lambda \mu; z \\ a \lambda \mu z \end{matrix} \right] \quad (8)$$

where $\phi^{(1)}[x, y]$ is the Appell function of first kind defined in [Slater² Chapter 9(9 11)]

Now summing the ${}_2\phi_1$ series on the right hand side of (8) by making use of the result [Slater², Appendix IV, IV-2, p. 247] we get the summation formulae

$$\phi^{(1)}[a, \lambda, \mu; a \lambda z, \mu z, z] = \frac{(\lambda \mu z, a z, q)_{\infty}}{(a \lambda \mu z, z; q)_{\infty}} \quad (9)$$

Taking $\lambda = 1/\mu$ in (9), we get

$$\phi^{(1)} [a, \mu^{-1}, \mu, az, \mu z, z] = 1 \quad (10)$$

Again taking $a = 1/\lambda \mu$ in (9), we get

$$\phi^{(1)} [(\lambda \mu)^{-1}; \lambda, \mu, z, \mu z, z] = \frac{(\lambda \mu z, z/\lambda \mu, q)_\infty}{(z; q)_\infty^2} \quad (11)$$

$$(b) \text{ Choosing } \Omega_n = \frac{(a, q\sqrt{a}, -q\sqrt{a}, b, c; q)_n}{(\sqrt{a}, -\sqrt{a}, aq/b, aq/c, aq/\lambda\mu; q)_n}$$

$$z = aq/bc\lambda \mu \quad \text{in (1)}$$

and making use of the summation formulae [Slater², Chapter III, eqn (3 3 1.3)], we get

$$\begin{aligned} & \phi \left[\begin{smallmatrix} (a, q\sqrt{a}, -q\sqrt{a}, b, c; \lambda, \mu, aq/bc\lambda, aq/bc\lambda\mu) \\ (\sqrt{a}, -\sqrt{a}, aq/b, aq/c, aq/\lambda\mu; -; -) \end{smallmatrix} \right] \\ &= \frac{(aq, aq/bc, aq/b\lambda\mu, aq/c\lambda\mu; q)_\infty}{(aq/b, aq/c, aq/\lambda\mu, aq/bc\lambda\mu; q)_\infty} \quad (12) \end{aligned}$$

Taking $\lambda = q^{-r}$, $\mu = q^{-r}$ in (12), we get

$$\phi \left[\begin{smallmatrix} a, q\sqrt{a}, -q\sqrt{a}, b, c; q^{-r}; q^{-s}; \frac{aq^{1+r}}{bc}, \frac{aq^{1+r+s}}{bc} \\ (\sqrt{a}, -\sqrt{a}, aq/b, aq/c, aq^{1+r+s}; -; -) \end{smallmatrix} \right]$$

$$= \frac{(aq, aq/bc, q)_{r+s}}{(aq/b, aq/c, q)_{r+s}} \quad (13)$$

As $b, c \rightarrow \infty$ in (12), we obtain

$$\begin{aligned} & \phi \left[\begin{matrix} a, q \sqrt{a}, -q \sqrt{a}; \lambda; \mu; aq/\lambda; aq/\lambda\mu \\ \sqrt{a}, -\sqrt{a}, aq/\lambda\mu; -; -; 2, 2, 1 \end{matrix} \right] \\ &= \frac{(aq, q)_\infty}{(aq/\lambda\mu; q)_\infty} \end{aligned} \quad (14)$$

Again taking $b, c \rightarrow \infty$ in (13), we get

$$\begin{aligned} & \phi \left[\begin{matrix} a, q \sqrt{a}, -q \sqrt{a}; q^{-r}; q^{-s}; aq^{1+r}, aq^{1+r+s} \\ \sqrt{a}, -\sqrt{a}, aq^{1+r+s}; -; -; \end{matrix} \right] \\ &= (aq, q)_{r+s} \end{aligned} \quad (15)$$

As $\lambda \rightarrow \infty$ in (14), we get

$${}_3\phi_2 \left[\begin{matrix} a, q \sqrt{a}, -q \sqrt{a}; -aq \\ \sqrt{a}, -\sqrt{a}; 3 \end{matrix} \right] = (aq; q)_\infty \quad (16)$$

Putting $a = 1$ in (16), we get the well known Euler identity

$$\sum_{r=0}^{\infty} (-1)^r q^{r(3r-1)/2} = (q; q)_\infty \quad (17)$$

Again taking $a = -1$ in (16), we get

$$\sum_{r=0}^{\infty} \frac{1+q^{2r}}{1+q^r} \frac{(-q; q)_r}{(q, q)_r} q^{r(3r-1)/2} = (-q; q)_{\infty} \quad (18)$$

(c) Choosing $\Omega_n = \frac{(a; q)_n}{(a\lambda\mu z q; q)_n}$ in (1) and making use of the summation formulae [Agarwal³, Appendix II formulae 13 for $c = 0$], we get

$$\phi^{(1)}[a; \lambda, \mu; a\lambda\mu z q, \mu z, z] =$$

$$\frac{(\lambda\mu z q, az q, q)_{\infty}}{(a\lambda\mu z q, z; q)_{\infty}} [1 - (a + \lambda\mu)z + a\lambda\mu z] \quad (19)$$

Taking $\lambda = 1/\mu$ in (19), we get

$$\phi^{(1)}[a; \mu^{-1}, \mu; az q, \mu z, z] = 1 \quad (20)$$

(d) Choosing

$$\Omega_n = \frac{(q^a, q)_n (q_1^b; q_1)_n (z q^{a+1} q_1^{b+1}; q q_1)_n (q, q)_n}{(z q^{a+1}; q)_n (z q_1^{b+1}; q_1)_n (z q^a b_1^b; q q_1)_n (\lambda\mu; q)_n}$$

in the identity (1) and making use of the summation formula [Agarwal³, Appendix II, formula 17] we get,

$$\begin{aligned} & \sum_{l,m=0}^{\infty} \frac{(q, q^a; q)_{l+m} (q_1^b; q_1)_{l+m} (z q^{a+1} q_1^{b+1}; q q_1)_{l+m}}{(\lambda\mu, z q^{a+1}; q)_{l+m} (z q_1^{b+1}; q_1)_{l+m}} \times \\ & \times \frac{(\lambda; q)_l (\mu; q)_m (\mu z)^l z^m}{(z q^a q_1^b; q q_1)_{l+m} (q; q)_l (q; q)_m} \end{aligned}$$

$$= \frac{(1-zq^a)(1-zq_1^b)}{(1-z)(1-zq^a q_1^b)} \quad (21)$$

Putting $q_1 = q$ in (21), we get

$$\sum_{l,m=0}^{\infty} \frac{(q, q^a; q^b, q)_{l+m} (\lambda; q)_l (\mu, q)_m (zq^{a+b+1}; q^2)_{l+m}}{(\lambda\mu, zq^{a+1}; zq^{b+1})_{l+m} (zq^{a+b}; q^2)_{l+m}} \times$$

$$\frac{(\mu z)^l z^m}{(q; q)_l (q; q)_m} = \frac{(a-zq^a)(1-zq^b)}{(1-z)(1-zq^{a+b})} \quad (22)$$

For $z = \frac{1}{q}$, (22) yields

$$\sum_{l,m=0}^{\infty} \frac{(q, q)_{l+m} (\lambda; q)_l (\mu, q)_m (q^{a+b+1}; q^2)_{l+m} \mu^l}{(\lambda\mu; q)_{l+m} (q^{a+b-1}; q^2)_{l+m} (q; q)_l (q; q)_m q^{l+m}}$$

$$= \frac{(1-q^{a-1})(1-q^{b-1})}{(1-q^{-1})(1-q^{a+b-1})} \quad (23)$$

(2) Putting q^2 for q in the identity (1) and then taking zq for z and

$$\Omega_n = \frac{(z^{-1}; q^2)}{(\lambda \mu z; q^2)_n}$$

Making use of the result [Verma and Jain⁴; (1.2)] we get the following summation formula :

$$\phi^{(1)} [z^{-1}; \lambda, \mu; \lambda \mu z; q^2; \mu z q; zq] = \frac{1}{2} \frac{(q, \lambda \mu; q^2)_{\infty}}{(\lambda \mu z, zq; q^2)_{\infty}} \times$$

$$\left\{ \frac{(z \sqrt{\lambda \mu}, q)_\infty}{(\sqrt{\lambda \mu}; q)_\infty} + \frac{(-z \sqrt{\lambda \mu}, q)_\infty}{(-\sqrt{\lambda \mu}, q)_\infty} \right\} \quad (24)$$

A number of other interesting results can also be scored

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